THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R

Volume XXII, No. 10

October, 1952

(A Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

152 West 42nd Street

New York 18, N. Y.

Printed in Great Britain

Annual subscription $95.00
Single issue 12.00

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THE CONSTANT OF ABSOLUTE CONTRACTION AND THE PERIODIC LAW

I. I. Zaslavsky and K. B. Yatsimirsky

The absolute contraction constant is the designation of the ratio of the molecular volume of a compound to the sum of the atomic volumes of its component elements:

$$C = \frac{Vm}{\Sigma V_A}$$

Many researches have has been devoted to the study of this magnitude. Earlier Beketov established the existence of a relation between the absolute contraction constant and the heat of formation of a compound [1]. One of us has established a relation between the contraction constant and the acid-base properties of compounds [2], and also their crystalline structure [3].

Recognizing that contraction is one of the characteristics of a substance most amenable to experimental determination, and bearing in mind the close link between the contraction constant and the totality of other physico-chemical properties, we resolved to follow the change in the values of the constant in question in a series of analogous compounds (oxides, sulfides, halides, etc.) with change in the atomic number of the element.

With the aim of obtaining comparative results we always utilized the contraction constants of the densest modifications and plotted the values only of those compounds whose valency exactly corresponds to the number of the group of the periodic system. The contraction constants of oxides (for this group of compounds it proved possible to obtain the fullest data), plotted in the order of magnitude of the atomic numbers of the elements, are shown in the diagram.

In the second and third periods the contraction constant of oxides as a rule increases with increasing atomic number of the element. Deviation from this rule is observed, however, in the case of N_2O_5, due evidently to the structural peculiarities of this compound; furthermore the contractions of P_2O_5 and SO_3 are almost identical.

In the fourth and fifth periods the contraction constant regularly increases from the first to the eighth group; starting from the first subgroup, it decreases to the fourth group and then again rises slowly.

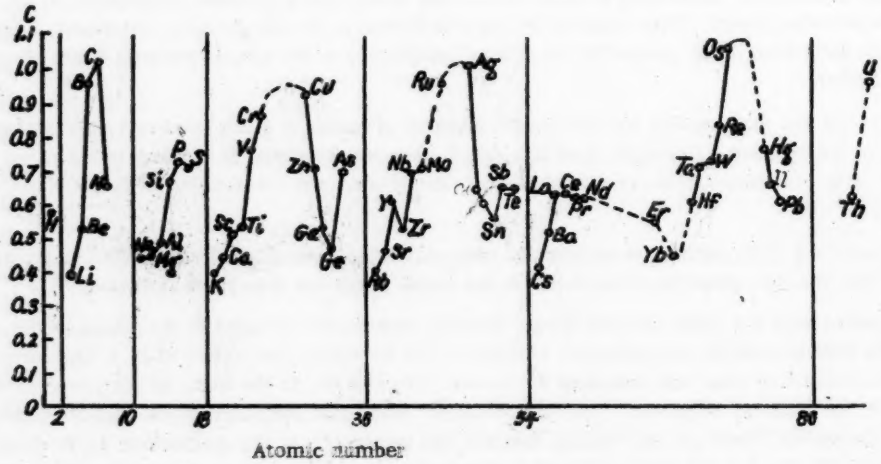
In connection with the appearance of these – hitherto unobserved – minima in the change of the contraction constant with the atomic number, it is pertinent to mention the following observation of D. I. Mendeleev [4]: ". . . the periods which find clear and complete expression, for example, in the forms of compounds, are complicated to some extent in the physical properties. Thus, for instance, apart from the maxima and minima corresponding to the periods and the groups, there are new special maxima and minima". In this connection, in the main groups of the periodic system [K, Ca, Sc, (Ti, Ge), As] there is observed a smooth increase in the contraction constant, i.e., approximately the same regularity is repeated as in the preceding periods.

In the fifth period a decline is observed in the contraction constant in passage from yttrium oxide to zirconium oxide. In the sixth period, however, the contraction constants of the lanthanides regularly decrease with increasing atomic number, evidently due to the well-known phenomenon of "lanthanide contraction". The contraction constant of HfO_2 is lower than that of La_2O_3. For the rest, the change of contraction constant is accompanied by the same regularity as in the two preceding periods. It is difficult to evaluate the change of contraction constant in the seventh period owing to the lack of an adequate amount of experimental material.

TABLE 1

Contraction and Electric Conductivity of Chlorides

LiCl 0.69 166	$BeCl_2$ 1.10 < 0.086	BCl_3 1.17 0	CCl_4 1.08 0	–
NaCl 0.67 133.5	$MgCl_2$ 0.86 28.8	$AlCl_3$ 0.91 $15 \cdot 10^{-6}$	$SiCl_4$ 1.07 0	PCl_5 > 1 0
KCl 0.60 103.5	$CaCl_2$ 0.87 51.9	$ScCl_3$ 0.93 15	$TiCl_4$ 1.13 0	VCl_5 ? 0
RbCl 0.60 78.2	$SrCl_2$ 0.77 55.7	YCl_3 0.98 9.5	$ZrCl_4$ 1.02 ?	$NbCl_5$ 1.04 $2 \cdot 10^{-7}$
CsCl 0.48 66.7	$BaCl_2$ 0.67 64.6	$LaCl_3$ 0.86 29.0	$HfCl_4$? ?	$TaCl_5$ 1.03 $2 \cdot 10^{-7}$
–	$RaCl_2$? ?	$AcCl_3$? ?	$ThCl_4$ 0.94 16	$PaCl_5$? ?



Contraction constants of higher oxides

As a rule the lowest contraction values are observed with typically ionic compounds (oxides of the alkali and alkali earth metals and oxides of lanthanides), whereas the highest values are observed with typical molecular compounds as well as with oxides of the eighth and adjacent groups where the characteristic features of the covalent type of bond are ever more prominently developed.

There is no doubt, therefore, that a definite close relationship exists between the type of chemical bond and the absolute contraction constant. This may be confirmed by a large amount of experimental material.

TABLE 2

Contraction Constants of Oxides and the Periodic Law
(for the Densest Modifications)

Li_2O 0.39	BeO 0.53	B_2O_3 0.96	CO_2 1.02	N_2O_5 0.66	–	–
Na_2O 0.44	MgO 0.45	Al_2O_3 0.49	SiO_2 0.67	P_2O_5 0.73	SO_3 0.72	Cl_2O_7 –
K_2O 0.40	CaO 0.45	Sc_2O_3 0.52	TiO_2 0.54	V_2O_5 0.77	CrO_3 0.87	Mn_2O_7 –
Rb_2O 0.41	SrO 0.46	Y_2O_3 0.61	ZrO_2 0.53	Nb_2O_5 0.70	MoO_3 0.72	Tc_2O_7 –
Cs_2O 0.42	BaO 0.52	La_2O_3 0.64	HfO_2 0.62	Ta_2O_5 0.72	WO_3 0.74	Re_2O_7 0.84
–	RaO –	Ac_2O_3 –	ThO_2 0.63	Pa_2O_5 –	UO_3 0.97	–

The electric conductivity of pure substances in the fused state is regarded as one of the most important criteria of the type of chemical bond in compounds. Biltz and Klemm [5] measured the electric conductivity of fused chlorides and on the basis of the experimental data they drew a line between compounds which conduct current and those which are nonconductors, ie. between those which are typically ionic and those compounds characterized by the presence of a covalent bond. Herein is reproduced the table generally appearing in textbooks of inorganic and physical chemistry and in geochemical literature (Table 1).

The left-hand columns of the table contain the absolute contraction constants and the line divides compounds formed with a low finite volume ($C < 1$) from compounds whose formation from the elements is accompanied by expansion. It was found that, with one exception ($AlCl_3$), the boundary line coincides with the line separating compounds that conduct current when melted from nonconductors. It may be noted that the increase of molecular volume of aluminum chloride when melted is slightly greater than that of other similar compounds. In the case of bromides and iodides the line demarcating compounds with $C<1$ from compounds with $C > 1$ passes lower and more to the left than in the case of chlorides, while with the corresponding fluorides it passes a little higher and a little more to the right.

On constructing a similar table for oxides (Table 2) it is found that the line dividing compounds with $C < 0.65$ from compounds with $C > 0.65$ is also the line which Fersman [6] considers to be the boundary between elements giving typical ions and those with molecular lattices.

The foregoing discussion also leads to the conclusion that to a certain extent the contraction constant may characterize the degree of polarization in chemical compounds. We know that the polarization of compounds with one and the same cation increases with increasing dimensions of the anion.

On this basis we can expect an increase of the contraction constants in the order of fluorides, chlorides, bromides and iodides, and also of oxides, sulfides, selenides and tellurides (in both cases the comparison is between compounds containing one and the same cation). Such a rise in contraction constants is actually observed in all known cases. It is also known that in compounds containing cations of the copper and zinc subgroup the polarization is stronger than in compounds of the alkali and alkali earth metals. This regularity is also confirmed on comparing the contraction constants of the corresponding compounds: The contraction constants of the subgroups are always higher than those of the analogous main groups. And the biggest difference is observed in the first group of the periodic system, the next biggest in the second group, followed by the difference in the third group. Finally in the fourth group such differences between the contraction constants of the main and subgroups have disappeared completely.

Pauling [7] showed that the heat of formation of chemical compounds in the standard state is higher the more pronounced is the ionic character of the compound. From this standpoint Beketov's [1] observation of the relation between contraction constant and heat of formation becomes understandable. The more pronounced is the ionic character of the bond in the compound in question, the smaller is the contraction constant, and the higher is the heat of formation of the compound.

The relation which we have established between the absolute contraction constant and the periodic law permits some additional conclusions about the geochemical characterization of the elements. It appears that elements forming oxides with higher contraction constants ($C > 0.95$) are the most frequently encountered

in nature in the native state. Elements forming oxides with lower constants (0.65-0.95) are found in nature either in the form of complex ions (W, Nb, Ta, etc.) or of sulfides (Hg, Zn, Cd, As, etc.). Elements whose oxides are characterized by maximum contraction during formation from simple starting materials ($C < 0.95$) are encountered in nature in the form of simple cations (K, Na, Ca, Sr, Ba, etc.).

SUMMARY

1. It is established that the absolute contraction constant of typical compounds of the elements (oxides, halides, sulfides, etc.) is a periodic function of the atomic numbers of these elements.

2. It is shown that to a certain extent the magnitude of the contraction constant can serve as a criterion of the character of the chemical bond in a given group of compounds. A correlation is established between contraction constant and electric conductivity of pure compounds, their polarizations and heats of formation.

3. A relation is demonstrated between the geochemical characteristic of elements and the contraction constant of their typical compounds.

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Received March 19, 1951

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POLAROGRAPHIC CHARACTERISTICS OF CADMIUM, LEAD AND THALLIUM IN AQUEOUS-ALCOHOLIC SOLUTIONS OF VARIOUS INDIFFERENT ELECTROLYTES

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Studies of the influence of a nonaqueous solvent on the polarographic characteristics of metallic ions can play an important part in the further development of both polarography and the theory of solutions. Nevertheless this problem has received little attention in the literature.

Researches in this direction with mixed solvents (including water-alcohol [1,2]) revealed firstly the continued validity of the expression $i_d = kC$, and secondly a drop in the value of the diffusion current with increasing content of the nonaqueous solvent but the constancy of the half-wave potential [2] has remained unexplained, as far as we can ascertain.

A series of investigations has been devoted to the polarographic behavior of various substances in absolute nonaqueous solvents. Many ions of heavy metals, for instance, have been studied in acetic acid [3]; alkali metals, thallium, ammonium, copper, and oxygen in liquid ammonia [4]; tin in methyl alcohol [5]; and cobalt, silver, arsenic and oxygen in pyridine (using a platinum microelectrode) [6]. The validity of the expression $i_d = kC$ could be confirmed for Pb, Cd, Zn, Co, Cr and Ni in acetic acid [3] and for Co and As in pyridine [6]. Half-wave potentials were also obtained in acetic acid and were found to be more negative than those in water. In many cases also, the reversibility was demonstrated of the reduction process, for instance for ions of the alkali metals, thallium, ammonium and copper ($Cu^{\cdot\cdot} \rightarrow Cu^{\cdot}$) in liquid ammonia [4] and for tin in methyl alcohol [5].

Finally reference may be made to the successful use by I. A. Korshunov [7] of mixed solvents for the purpose of amperometric titration.

The aim of the present investigation is the study of the dependence of the magnitude of the half-wave potential on the diffusion current of cadmium, lead and thallium and on the content of ethyl alcohol in aqueous-alcoholic solutions of various indifferent electrolytes.

EXPERIMENTAL

The solutions were prepared from analytically pure $Cd(NO_3)_2$ ($1 \cdot 10^{-3}$ molar), $Pb(NO_3)_2$ ($2 \cdot 10^{-3}$ molar) and $TlNO_3$ ($1 \cdot 10^{-3}$ molar). Use was made as indifferent electrolytes of KNO_3 (0.1 molar), NH_4NO_3 (0.1 and 0.9 molar), NH_4Cl (0.9 molar) and KI (0.9 molar). Maxima were suppressed by addition to the solution of 0.01% gelatin. The aqueous-alcoholic solvent was prepared from absolute ethanol. Solvents containing 20, 45 and 65% (by volume) of alcohol were investigated. Comparison polarograms in water were plotted. Polarographic determination was performed with the help of a visual polarograph (Gorki University model) supplemented by a sliding-contact potentiometric set-up. A saturated calomel electrode was used as the nonpolarizing anode. Measurements were made at a temperature of $25 \pm 0.2°C$. Volatilization of solvent on passage of a hydrogen stream proved to be so slight that it was not necessary to saturate the hydrogen beforehand with the vapor of the solvent.

The characteristics of the capillary used in the investigation are shown in Table 1. It is seen that increasing alcoholic content is accompanied in line with the measurements of Zanko and Manusova [2], with a slight reduction in the dropping period (τ). The weight of mercury discharged in unit time (m) remains independent of the nature of the solvent in agreement with the observations of Kolthof and Lingane [8].

The resistance of the polarographic electrolyzer was determined from the difference of the half-wave potentials corresponding to the difference (1:10) of concentrations of the reduced ion [9]. With increasing

TABLE 1

C_2H_5OH (%)	(0.1-0.9 m NH_4NO_3(KNO$_3$)) $m_{comp.}$ (mg/sec^{-1})	$\tau_{comp.}$ (sec.)	$m^{2/3}\tau^{1/6}$ (mg$^{2/3}$/sec$^{-1/2}$)	0.9 m KI m_{comp} (mg/sec^{-1})	$\tau_{comp.}$ (sec.)	$m^{2/3}\tau^{1/6}$ (mg$^{2/3}$/sec$^{-1/2}$)	0.9 m NH_4Cl $m_{comp.}$ (mg/sec^{-1})	$\tau_{comp.}$ (sec.)	$m^{2/3}\tau^{1/6}$ (mg$^{2/3}$/sec$^{-1/2}$)
0	1.338	4.00	1.53	1.338	3.69	1.51	1.338	3.92	1.52
20	1.338	3.85	1.52	1.338	3.70	1.51	1.338	3.80	1.52
45	1.338	3.75	1.51	1.338	3.58	1.50	1.338	3.71	1.51
65	1.338	3.75	1.51	1.338	3.66	1.50	1.338	3.63	1.50

alcohol content the resistance of the solution increased considerably. Thus, for example, when the aqueous solution of 0.1 M NH_4NO_3 exhibited a resistance of 1000 ohms, the corresponding aqueous-alcoholic solution with 65% alcohol content had a resistance of approximately 3500 ohms.

The accuracy of the potential of the calomel electrode was checked against the half-wave potential of thallium in 1 N KNO_3 [8].

In addition to the plotting of the respective polarograms, the obtained results were represented graphically in a plot of π against $\log\frac{i}{i_d - i}$, which permitted the determination of the reversibility of the reduction process and also the precise determination of the half-wave potential. An example of diagrams of this type is Figure 1, which represents the results of polarographic measurements on lead and thallium in 0.1 M KNO_3 and of cadmium in 0.9 M KI. The half-wave potentials and angular coefficients of the straight-line plots obtained from Figure 1 and other similar graphs are summarized in Table 2. Also the half-wave potentials are plotted as functions of the alcohol content in Figure 2.

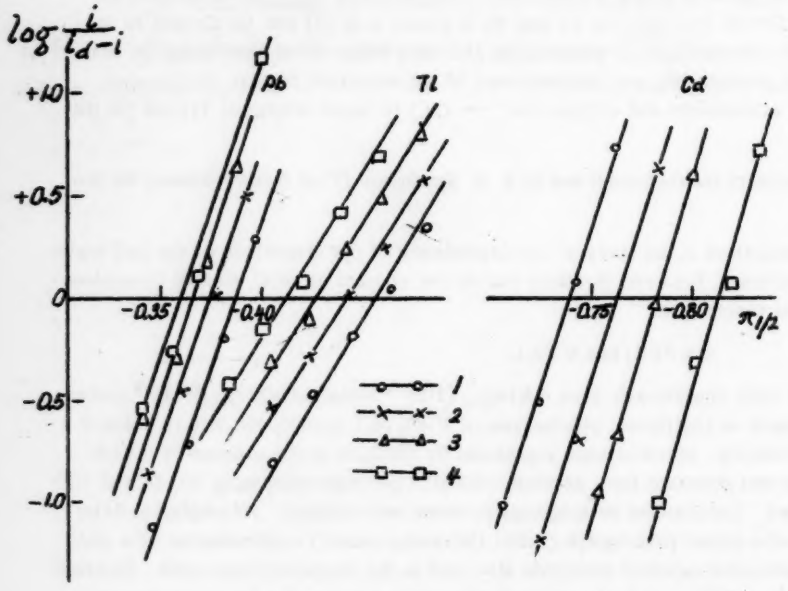

Figure 1. Check of the equation of the polarographic wave of lead and thallium in aqueous-alcoholic solutions of 0.1 M KNO_3, and of cadmium in aqueous-alcoholic solutions of 0.9 M KI.
1 - 0% C_2H_5OH; 2 - 20% C_2H_5OH; 3 - 45% C_2H_5OH; 4 - 65% C_2H_5OH.

The values of the diffusion currents (i_d) and of the diffusion current constants $I_D = \frac{i_d}{m^{2/3}\tau^{1/6}C}$ are presented in Table 3 and Figure 3. The values of I_D of solutions $2 \cdot 10^{-3}$ M $Pb(NO_3)_2$ and of $1 \cdot 10^{-3}$ M $TlNO_3$ in 0.9 M NH_4Cl at an alcohol content $\geqslant$ 45% in the case of lead and $\geqslant$20% in the case of thallium were not calculated since these solutions proved to be saturated in relation to chlorides of lead and thallium. The solubility of $PbCl_2$ and of TlCl under the stated conditions was not determined.

Evaluation of Results

We consider in the first place the question of the possible influence of the diffusion potentials on the accuracy of the half-wave potentials measured by us. This point is dealt with by A.L. Brodsky [10] who carried out a detailed investigation of various galvanic chains using aqueous-alcoholic solvents. This author's data justify the assumption that the diffusion potentials had only a very slight effect upon our results. The effect is of the same order (approx. 1 mV) as the accuracy of measurement of the half-wave potentials, so that it may be neglected.

TABLE 2

Half-Wave Potentials of Cd, Pb and Tl in Aqueous-Alcoholic Solutions of Various Indifferent Electrolytes

C_2H_5OH (%)	Cd								Pb			
	0.1 M NH_4NO_3		0.9 M NH_4NO_3		0.9 M NH_4Cl		0.9 M KI		0.1 M KNO_3		0.9 M NH_4Cl	
	$\pi^{1/2}$ (volt)	angular coeffi-cient	$\pi^{1/2}$ (volt)	angular coeffi-cient	$\pi^{1/2}$ (volt)	angular coeffi-cient	$\pi^{1/2}$ (volt)	angular coeffi-cient	$\pi^{1/2}$ (volt)	angular coeffi-cient	$\pi^{1/2}$ (volt)	angular coeffi-cient
0	-0.583	0.035	-0.590	0.034	-0.641	0.029	-0.740	0.030	-0.387	0.034	-0.433	0.034
20	-0.571	0.034	-0.578	0.034	-0.641	0.030	-0.763	0.030	-0.375	0.034	-0.428	0.034
45	-0.560	0.034	-0.569	0.035	-0.650	0.030	-0.784	0.030	-0.366	0.034	-0.433	0.034
65	-0.549	0.034	-0.555	0.035	-0.675	0.030	-0.815	0.032	-0.361	0.035	-0.449	0.030

TABLE 2 -- (continued)

C_2H_5OH (%)	Tl			
	0.1 M KNO_3		0.9 M NH_4Cl	
	$\pi^{1/2}$ (volt)	angular coeffi-cient	$\pi^{1/2}$ (volt)	angular coeffi-cient
0	-0.455	0.060	-0.483	0.059
20	-0.442	0.064	-0.469	0.059
45	-0.426	0.063	-0.466	0.059
65	-0.412	0.062	-0.461	0.058

TABLE 3

Diffusion Currents i_d and Diffusion Current Constants I_D, Cd, Pb and Tl in Aqueous-Alcoholic Solutions of Various Indifferent Electrolytes

C_2H_5OH (%)	Cd							
	0.1 M NH_4NO_3		0.9 M NH_4NO_3		0.9 M NH_4Cl		0.9 M KI	
	i_d, μA	I_D	i_d, μA	I_D	i_d, μA	I_D	i_d, μA	I_D
0	6.00	3.9	6.24	4.1	6.34	4.2	6.54	4.3
20	4.62	3.0	4.69	3.1	5.28	3.5	5.08	3.4
45	3.83	2.5	4.02	2.7	4.49	3.0	4.46	3.0
65	3.53	2.3	3.70	2.4	4.22	2.8	4.46	3.0

TABLE 3 -- (continued)

C_2H_5OH (%)	Pb				Tl			
	0.1 M KNO_3		0.9 M NH_4Cl		0.1 M KNO_3		0.9 M NH_4Cl	
	i_d, μA	I_D	i_d, μA	I_D	i_d, μA	I_D	i_d, μA	I_D
0	12.8	4.2	14.2	4.7	4.75	3.1	4.54	3.0
20	10.10	3.3	11.08	3.6	3.83	2.5	2.44	–
45	8.45	2.7	3.70	–	3.17	2.1	1.43	–
65	7.78	2.6	1.58	–	2.81	1.9	0.69	–

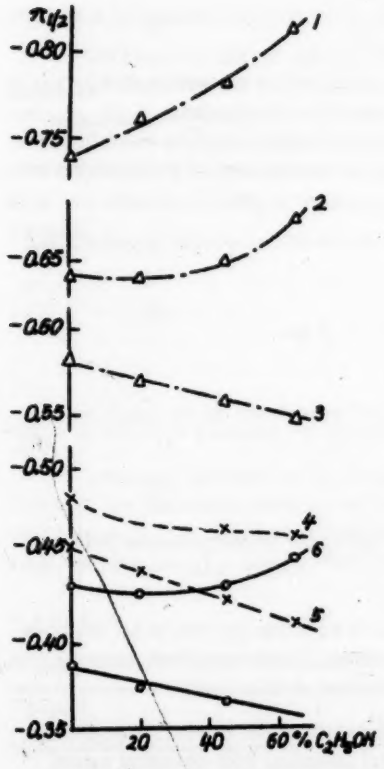

Figure 2. Dependence of the half-wave potential of cadmium, lead and thallium on the alcohol content in aqueous-alcoholic solutions of various indifferent electrolytes.
1 - Cd in 0.9 M KI; 2 - Cd in 0.9 M NH_4Cl; 3 - Cd in 0.1 M NH_4NO_3; 4 - Tl in 0.9 M NH_4Cl; 5 - Tl in 0.1 M KNO_3; 6 - Pb in 0.9 M NH_4Cl; 7 - Pb in 0.1 M KNO_3.

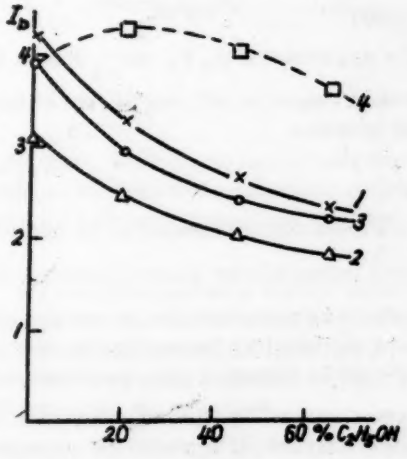

Figure 3. Dependence of the diffusion current constant on the alcohol content in the aqueous-solvent.
1 - Pb in 0.1 M KNO_3; 2 - Tl in 0.1 M KNO_3; 3 - Cd in 0.1 M NH_4NO_3; 4 - ditto with correction for the change of viscosity.

The determination of the angular coefficients of the straight lines representing the dependence of the potential π on the $\log\frac{i}{i_d-i}$ (Table 2) shows that in all the cases under consideration the angular coefficient was close to the theoretical value of $2.3\frac{RT}{nF}$ [8]. It is necessary to emphasize that the correct value of the angular coefficient was only obtained after a correction had been applied to all the points on the polarographic wave which took into account the voltage drop in the electrolyzer. The agreement between the theoretical and experimental angular coefficients permits us to draw the conclusion that regardless of the alcohol content the process of reduction of Cd^{++}, Pb^{++} and Tl^{+} proceeds reversibly at the dropping mercury electrode.

The half-wave potentials of cadmium, lead and thallium in the investigated indifferent electrolytes (Table 2, Figure 2) changed with changing content of alcohol in opposition to the conclusions of A.M. Zanko and F. A. Manusova [2]. In solutions of $NH_4NO_3(KNO_3)$ the half-wave potentials of cadmium, lead and thallium become more positive with increasing alcohol content; the same is true of the half-wave potentials of thallium in NH_4Cl solutions; on the other hand in NH_4Cl and KI solutions the half-wave potentials of cadmium and lead are shifted in the direction of negative values.

For the purpose of clarifying the cause of this phenomenon we shall first consider indifferent electrolytes in which complex formation does not occur. Among the solutions which we have examined, this condition is met by solutions of $NH_4NO_3(KNO_3)$. As illustrated by the case of cadmium (Table 2) a nearly tenfold change of NH_4NO_3 concentration has very little effect on the magnitude of the half-wave potential. This is observed in all cases regardless of the alcohol content and is only possible in the absence of complex formation.

Considering the above-noted reversibility of the process of reduction of Cd^{++}, Pb^{++}, and Tl^{+}, the half-wave potentials of these ions in the absence of complex formation may be determined from the following thermodynamic equation [8]:

$$(\pi_{i/2})_S = \pi_0 + \pi_S + \frac{0.059}{n}\log C_{saturated}\, f_{saturated} - \frac{0.059}{n}\log\frac{f_a k_S}{f_S k_a}, \qquad (1)$$

where π_0 is the normal potential of the metal; π_S is the e.m.f. of the system metal-saturated amalgam; $C_{saturated}$ is the solubility of the metal in mercury; f_a is the activity coefficient of the metal in the amalgam; $f_{saturated}$ is the same coefficient when the amalgam is saturated with metal; f_S is the activity coefficient of the metallic ions in solution; k_S is the diffusion current constant; k_a is a constant proportional to the square root of the diffusion coefficient of metallic atoms in the amalgam.

Equation (1) may be rewritten thus if all the terms independent of the nature of the solvent are substituted by the term "const":

$$(\pi_{i/2})_S = \text{const.} + \pi_0 - \frac{0.059}{n}\log\frac{k_S}{f_S}. \qquad (2)$$

The magnitudes of π_0, k_S, and f_S depend on the nature of the solvent.

Brodsky's equation [10] may be applied for determination of the effect of the solvent on the magnitude of the normal potential:

$$\pi_0 = A \pm \frac{B}{D}, \qquad (3)$$

where A is a magnitude independent of the nature of the solvent; $B = \frac{en_i}{2a_i}$ (n_i and a_i are respectively the valence and the ionic radius), D is the dielectric constant of the solvent.

It should be pointed out that in Brodsky's paper [10] a plus sign appears in equation (3); but in his textbook on Physical Chemistry [11] the equation contains a minus sign. Generally speaking, in our view, both signs are possible, the choice depending upon the charge on the outer surface of the electrical double layer.

Having assumed, to a first approximation, that a_i is independent of the nature of the solvent, it is possible on the basis of equation (3) to predict the character of the change of the normal potential with changing nature of the solvent. In the case of cadmium, lead and thallium, when the charge on the outer surface of the electric double layer is positive (with an ionic activity equal to 1), the normal potential of these metals must change in the positive direction with increasing alcohol content of the aqueous-alcoholic solvent since the dielectric constant of the solvent will fall at the same time. According to Brodsky [10] in similar conditions the normal potential of the mercury electrode is shifted in the direction of negative values, which is also in conformity with equation (3) if we take into account the negative charge of the outer surface of the electric double layer and, consequently, the negative sign in equation (3).

Let us now return to consideration of equation (2). It follows from this equation that the character of the change of the half-wave potentials of the simple ions Cd^{++}, Pb^{++} and Tl^{+} with changing content of alcohol in aqueous-alcoholic solvents must be governed by the character of the change of three magnitudes: the normal potential (π_0), the diffusion current constant (k_S) and the activity coefficient of the ion undergoing reduction (f_S). As already noted, the first of these magnitudes (the normal potential of cadmium lead and thallium) will be shifted in the positive direction with increasing alcohol content, while the diffusion current constant (k_S) will decrease (Table 3); the ionic activity coefficient (f_S) will also decrease at the same time as the dielectric constant of the solution.

We have seen (Figure 2) that the half-wave potentials of Cd^{++}, Pb^{++} and Tl^{+} in aqueous alcoholic solutions of $NH_4NO_3(KNO_3)$ change in the direction of positive values with increasing alcohol content. Even, therefore, with a possible increase in the value of $\frac{k_S}{f_S}$, the effect of increasing alcohol content on the half-wave potential is smaller than the effect of the shift of the normal potential of the metal in the positive direction.

The validity of the above equation (3) of Brodsky has been experimentally confirmed both by the author and by other workers [11]. It is easy to show that our polarographic results for cadmium, lead and thallium in aqueous-alcoholic solutions of $NH_4NO_3(KNO_3)$ can also be utilized for quantitative checking of Brodsky's equation. In fact, on substituting in equation (2) the value of the normal potential in equation (3) we get:

$$(\pi_{1/2})_S + \frac{0.059}{n} \log \frac{k_S}{f_S} = (\pi_{1/2})_{S\ corr.} = \text{const}. + \frac{B}{D} . \qquad (4)$$

If we assume, as noted above, that a_1 in equation (3) is independent of the nature of the solvent, then it follows from equation (3) that if Brodsky's equation is valid the corrected half-wave value $(\pi_{1/2})_{S\ corr.}$ must be a rectilinear function of $\frac{1}{D}$.

We have calculated the corrected values of the half-wave potentials of cadmium, lead and thallium in 0.1 M KNO_3. For this purpose we calculated the corresponding activity coefficients (f_S) in aqueous-alcoholic solution of 0.1 M KNO_3 at various contents of alcohol. The problem was solved more accurately in the case of thallium, since we know from the literature data [12] that the activity coefficient of Tl in solution with excess of KNO_3 is substantially equal to the activity coefficient of KNO_3. Now we have found the activity coefficients of 0.1 M solution of KNO_3 with various dielectric constants of the solvent from the well-known Debye-Huckel formula:

$$\log f_S = - \frac{250 \cdot n^2 \cdot D^{-\frac{3}{2}} \sqrt{I}}{1 + 2.06 \cdot b_1 D^{-\frac{1}{2}} \sqrt{I}} \qquad (5)$$

whose accuracy is adequate for our purpose.

Assuming the value of b_1 in equation (5) equal to 0.43 A (for KNO_3, according to Dol [13] and the values of the dielectric constants of Table 4 (after Brodsky [10]), then on the basis of the calculated activity coefficients (f_S) we find from equation (4) (left-hand side) the corrected half-wave potentials of thallium. Here we take $(\pi_{1/2})_S$ and k_S from Tables 2 and 3 respectively.

TABLE 4

Dielectric Constants of Aqueous-Alcoholic Solutions

C_2H_5OH (Vol.- %)	0	20	45	65
D	81.7	70.5	56.6	44.9

We have been unable to find any experimental data in the literature for the activity coefficients of cadmium and lead in KNO_3 solution. We therefore only carried out a rough evaluation of these activity coefficients from the expression:

$$\frac{\log f_{Tl^+}}{\log f_{Cd^{++},\ Pb^{++}}} = \frac{n^2_{Tl^+}}{n^2_{Cd^{++},\ Pb^{++}}} = \frac{1}{4} ,$$

applying the activity coefficients of thallium found from equation (5). Subsequent calculations of the corrected half-wave potentials of cadmium and lead were made as for thallium.

Results of the check of equation (4) are represented in Figure 4 (curve 2). A comparison plot of $(\pi_{1/2})_S$ against $\frac{1}{D}$ is also shown (curve 1).

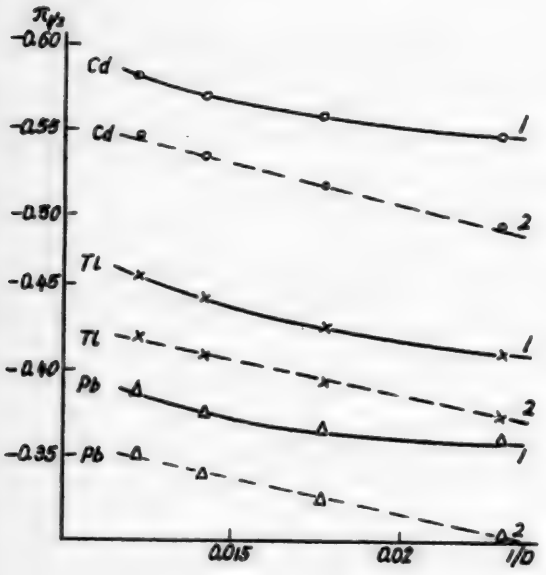

Figure 4. Dependence of the half-wave potential on the dielectric constant of the solvent. Solvent: 0.1 M $KNO_3(NH_4NO_3)$. Curve 1) $\pi_{1/2}$ versus 1/D; Curve 2) $\left(\pi_{1/2} + \frac{0.059}{n} \log \frac{k_S}{f_S}\right)$ versus 1/D.

We see from Figure 4 that the relation between $(\pi_{1/2})_{S_{corr.}}$ and 1/D for cadmium, lead and thallium is substantially rectilinear; the small concavity (also found on similar curves in Brodsky's paper) is readily explained by our assumption of the independence of the ionic radius on the nature of the solvent. Brodsky [10] also drew attention to this.

From the foregoing considerations we reach the conclusion that the results of polarography of cadmium, lead and thallium in 0.1 M KNO_3 (NH_4NO_3) confirm the validity of Brodsky's theoretical equation which formulates the dependence of the normal potential of a metal on the nature of the solvent.

The numerical values of B in equation (4) are the corresponding angular coefficients of the straight lines in Figure 4. We can therefore calculate the ionic radii of $Cd^{\cdot\cdot}$, $Pb^{\cdot\cdot}$ and $Tl^{\cdot}$, and these are found to be: $a_{Cd^{\cdot\cdot}} = 3.1$ A, $a_{Pb^{\cdot\cdot}} = 3.4$ A and $a_{Tl^{\cdot}} = 1.9$ A.

We shall now consider the values found for the half-wave potentials of cadmium, lead and thallium in aqueous-alcoholic solutions of NH_4Cl and of cadmium in KI. We know that complex formation occurs even in aqueous solutions of NH_4Cl and KI.

The half-wave potential during reversible reduction of complex ions may be expressed by the following equation [8]:

$$(\pi_{1/2})_C = (\pi_{1/2})_S + \frac{0.059}{n} \log \frac{f_C k_S}{f_S k_C} + \frac{0.059}{n} \log K_C - p \frac{0.059}{n} \log C_x f_x, \quad (6)$$

where k_C is the dissociation constant of the complex ion; p is the coordination number; C_x and f_x are the concentration and the activity coefficient of the complex-former; k_C and f_C are the diffusion current constant of the complex ion and its activity coefficient.

Substituting in this equation the value $(\pi_{1/2})_S$ in equation (2) and putting $\frac{f_C k_S}{f_S k_C} \cong 1$, we get:

$$(\pi_{1/2})_C = \text{const.} + \pi_0 - \frac{0.059}{n} \log \frac{k_S}{f_S} + \frac{0.059}{n} \log K_C - p \cdot \frac{0.059}{n} \log C_x f_x. \quad (7)$$

With the exception of the constant C_x, and possibly, p, all the terms in equation (7) depend on the nature of the solvent.

The dissociation constant of the complex ion (K_C) must all with transition from aqueous to aqueous-alcoholic solutions with a lower dielectric constant. This leads, as seen from equation (7), to a shift of the half-wave potential in the direction of negative values. A shift in the same direction also occurs due to possible rise in the value of k_S/f_S with increasing alcohol content; a reverse effect on the magnitude of the half-wave potential is exercised by the change of normal potential (π_0) and of the activity coefficient of the complex-former (f_x).

It follows from our experimental data (Figure 2) that in the case of cadmium and lead in 0.9 M NH_4Cl at high alcohol concentrations and in the case of cadmium in 0.9 M KI at any alcohol concentration, the half-wave potential is shifted in the negative direction with increasing concentration of alcohol. This points to a predominant influence of the factor of reduction of the value of the dissociation constant of the complex ion with increasing alcohol content (7); in this connection a steeper course of curve (Figure 2) is obtained with cadmium (especially in 0.9 M KI), i.e. in this case addition of alcohol causes a sharper fall in the dissociation constant of the complex ion.

Low concentrations of alcohol in solutions of cadmium and lead in 0.9 M NH_4Cl bring about (Figure 2) a small change of half-wave potential with changing alcohol content; this is due to the approximately equal but opposite effect of other factors on the half-wave potential. Figure 2 shows that the half-wave potential of thallium in 0.9 M NH_4Cl is shifted to the negative side with increasing alcohol concentration; the course of the curve is here steeper than in corresponding KNO_3 solutions, evidently as a result, likewise, of complex-formation which is characterized by a slight fall in dissociation constant with increasing alcohol content.

In the present case we cannot draw any quantitative conclusions owing to the lack of experimental material for complex ions in an aqueous-alcoholic solvent.*

We shall now analyze the effect of an aqueous-alcoholic solvent on the magnitude of the diffusion current.

Table 3 and Figure 3 show that the magnitudes of the diffusion currents of cadmium, lead and thallium decrease with increasing alcoholic content. These results are in agreement with those of other authors [1,2].

We attempted to establish to what degree the fall in value of the diffusion current is associated with the fall in ionic diffusion coefficient with increasing viscosity of the solution when alcohol is added. Calculation of the change of diffusion current constant with change of viscosity was carried out with the help of the equations of Stokes-Einstein and Ilkovič [9]. The final expression for obtaining the corrected value of the diffusion current constant ($I_{D_{corr.}}$) had the form:

$$I_{D_{corr.}} = I_D \sqrt{\frac{\eta}{\eta_{H_2O}}}, \qquad (8)$$

where I_D is the observed diffusion current constant in the mixed solvent; η is the viscosity coefficient of the mixed solvent; η_{H_2O} is the viscosity coefficient of water.

Making use of the corresponding I_D values in Table 3 and Landolt's viscosity coefficients [14], we obtained the corrected diffusion current constants from equation (8). Results of these calculations for cadmium are plotted in Figure 3 (curve 1). The lead and thallium curves have a similar shape, i.e. they differ from the expected straight line parallel to the abscissas. Nevertheless we see from the cadmium data (Figure 3, curve 1) that the fall in diffusion current constant with increasing alcohol content of the solution proceeds mainly at the expense of a drop in the viscosity coefficient. When analyzing these results we must not forget the slight inaccuracy involved in applying the Stokes-Einstein equation to the case of ionic diffusion.

In conclusion we may note that the very low solubility of lead and thallium salts in aqueous-alcoholic solutions of NH_4Cl, particularly with alcohol contents $\geqslant$ 50% (Table 3) and the considerably higher solubility of cadmium salts in similar solutions create the possibility of polarographic determination in the medium in question of small concentrations of cadmium in presence of a large excess of lead and thallium.

SUMMARY

1. The polarographic characteristics of cadmium, lead and thallium in aqueous-alcoholic solutions of KNO_3, NH_4NO_3, NH_4Cl and KI have been investigated.

2. In all cases, regardless of the alcohol content, reversibility of the process of reduction of cadmium, lead and thallium at the dropping mercury electrode was observed.

3. It is shown that the magnitudes of the half-wave potentials of cadmium, lead and thallium in all the investigated indifferent electrolytes changed with changing content of alcohol, in opposition to the conclusions

* See our next communication.

of A. M. Zanko and F. A. Manusova [2].

4. In the absence of complex formation (KNO_3, NH_4NO_3) the half-wave potentials of cadmium, lead and thallium changed in the direction of negative values with increasing alcohol content; when complexes were formed, e.g. with cadmium in NH_4Cl and particularly KI, the increase of alcohol concentration may cause a considerable shift of the half-wave potential in the negative direction. The character of the observed change in the half-wave potentials was analyzed with reference to the effect of change of magnitude of the normal potential, the dissociation constant of the complex ion and other factors.

5. On the basis of the polarographic data for cadmium, lead and thallium in aqueous-alcoholic solutions of 0.1 M KNO_3 (NH_4NO_3) it was possible to confirm the validity of Brodsky's equation [10] for these metals. This equation expresses the relation between the normal potential and the dielectric constant of the solvent.

6. A fall is observed in the diffusion current constants of cadmium, lead and thallium with increasing content of alcohol in the solution. This is bound up—as shown by calculations using the Stokes-Einstein and Ilkovič equations—mainly with a fall in the viscosity coefficient of the solvent.

7. The suitability is demonstrated of an aqueous-alcoholic solution of NH_4Cl as a medium for polarographic determination of small concentrations of cadmium in presence of excess of lead and thallium.

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Received May 4, 1951

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THERMOCHEMISTRY OF NICKEL AMMINE COMPLEXES IN AQUEOUS SOLUTION

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The study of nickel ammine complexes in aqueous solution is of interest both for inorganic and analytical chemistry.

Nickel ammine complexes have been known for a long time [1] and have been studied by many workers, but the process of their formation in solution has received little attention. In particular, data are lacking on the thermochemistry of nickel ammine solutions. Only one determination has been reported [2] for the heat of formation of a solution of $[Ni(NH_3)_6]Cl_2$ [2].

The equilibria in solutions in concentrated ammonia have likewise not been adequately investigated. Fairly accurate data exist for complexes of the type of $[Ni(NH_3)_n]^{2+}$ (n = 1,2,3,4) but for complexes with a larger number of addenda ($n > 4$) the data are unreliable [3,4].

The purpose of the present investigation is the study of the thermochemistry and, to some extent, the thermodynamics of nickel ammine solutions.

EXPERIMENTAL

We made use of the previously described apparatus and procedure [5] for the determination of the heats of mixing.

The heat of mixing of $NiCl_2$ solutions with ammonia solutions of different concentrations was determined.

A weighed amount of $NiCl_2$ solution was placed in a glass ampoule onto the side of which was blown a small glass bulb. The vessel was then placed in a calorimeter. Experiments were made with solutions containing about 0.25 g $NiCl_2$ per g of solution; the latter was prepared by dissolving pure $NiCl_2$ in water. The calorimeter was charged with ammonia solutions of various concentrations from 0.5 M to 7.5 M. After a uniform temperature had been established, the ampoule was crushed against the side wall of the calorimeter in the upper part of the space filled with the calorimetric liquid. All measurements were made at the temperature of the outer casing ($25.00 \pm 0.05°$) using a Bechmann thermometer whose entire scale covered one degree, so that the accuracy of reading reached $\pm 0.0002°$. The radiation correction was made graphically.

The weight of the calorimetric liquid was determined with an accuracy of ± 0.5 g. The error of determination of the aqueous components was about $\pm$ 0.5 g.

The heats of mixing found are listed in Table 1.

The data of Table 1 show that the heat of mixing changes with the ammonia concentration and approaches a constant value with increasing NH_3 concentration. As a check on the obtained heats of mixing we performed an experiment on the determination of the heats of solution of the solid salt $[Ni(NH_3)_6]Cl_2$ in NH_3 solutions with concentrations of 0.5 M to 1 M. In the determination of the heat of solution of the solid salt $[Ni(NH_3)_6]Cl_2$ we made use of the apparatus and method used above. About 1-1.5 g of the solid salt (nickel hexammine chloride) was taken.
Heat of solution values are given in Table 2.

On the basis of the experimental data for the heats of mixing we have calculated the equilibrium constant of the reaction:

$$[Ni(NH_3)_4]^{2+}_{aq.} + 2NH_3\ aq. \rightleftharpoons [Ni(NH_3)_6]^{2+}_{aq.} \qquad (1)$$

on the assumption that the formation of the $[Ni(NH_3)_6]^{2+}$ ion proceeds according to the scheme shown.

We confirmed the obtained value of the constant by determinations by the solubility method.

Up to now the equilibrium constant has been determined by the solubility method by measuring the solubility of the simple salt in solutions of the addendum. We determined the equilibrium constant from the solubility of the complex salt $[Ni(NH_3)_6]I_2$ in ammonia solutions of various concentrations. The flask containing the solid salt $[Ni(NH_3)_6]I_2$ in ammonia solution was shaken for several days at a temperature of $25.00 \pm 0.05°$. After equilibrium had been reachedthe solutions were analyzed for the content of iodine ion.

TABLE 1

Heat of Mixing of Solutions of $NiCl_2$ with Ammonia Solutions of Various Concentrations

No. of Expt.	Concentration: NH_3 (in moles per liter)	Concentration: $NiCl_2$ solution ($NiCl_2$ in 1 g solution)	Temp. (°C) change with radiation correction	Radiation Correction (°C)	Weight of $NiCl_2$ in g	Heat capacity of the calorimeter (in cal.)	Heat of mixing (in kcal)
1	0.47	0.2510	0.5169	0.0073	2.1020	557.8	17.78
2	0.65	0.1878	0.3903	0 0067	1.5070	559.0	18.76
3	0.95	0.2510	0.6521	0 0041	2.3960	556.8	19.65
4	1.17	0.1105	0.1697	0.0067	0.6104	556.8	20.06
5	1.28	0.1878	0.3925	0.0053	1.3810	555.0	20.44
6	2.46	0.2439	0.3502	0.0098	1 0940	551.8	22.80
7	3.60	0.2196	0.4355	0.0047	1.2900	546.5	23.94
8	4.65	0.2439	0.4475	0.0134	1.2600	544.0	25.04
9	5.21	0.2463	0.4339	0.0183	1.2060	546.5	25.48
10	6.24	0.2463	0.5190	0.0018	1.4180	537.6	25.50
11	7.50	0.2463	0.4565	0.0057	1.2160	533.8	25.97

TABLE 2

Heat of Solution of $[Ni(NH_3)_6]Cl_2$ in Ammonia Solutions

	Conc. of NH_3 in moles per liter	Weight of $[Ni(NH_3)_6]Cl_2$ (in g)	Change of temp. (in °C) with radiation correction)	Correction for radiation (in °C)	Heat capacity of calorimeter (in cal)	Heat of solution (in Kcal)
1	0.70	1.0626	0.08519	−0.0407	558.0	−10.40
2	0.50	1.3767	0.1267	0.0000	558.8	−11.92

TABLE 3

Solubility of $[Ni(NH_3)_6]I_2$ in Solutions of Ammonia of Various Concentrations

	NH_3 conc. (in moles per liter)	Solubility of $[Ni(NH_3)_6]I_2$ (in moles per liter)	Concentration of $[Ni(NH_3)_6]^{2+}$	Equilibrium constant of reaction (1)
1	0.25	0.02858	0.001683	1.04
2	0.47	0.02086	0.003160	1.82
3	0.70	0.01626	0.005200	0.96
4	0.97	0.01429	0.006730	0.94
5	1.70	0.01248	0.008828	0.84
6	2.58	0.01172	0.01001	0.88
7	3.39	0.01150	0.01040	0.82
8	4.50	0.01117	–	–
9	7.40	0.01111	–	–
10	8.70	0.01111	–	–
11	10.50	0.01111	–	–
12	12.12	0.01113	–	–

The results are shown in Table 3.

Evaluation of Results

We see from the data of Table 1 that the heat of mixing increases with increasing ammonia concentration and approaches a limit. This behavior suggests that more dilute ammonia solutions contain a few complex ions with a different number of combined molecules of ammonia. With increasing ammonia concentration the proportion of complexes with a smaller ammonia content decreases and only one complex ion begins to preponderate in the solution. The limiting value approached by the heat of mixing is 26 kcal and we assumed this to be the heat of formation of the $[Ni(NH_3)_6]^{2+}$ ion from the Ni^{2+} ion and ammonia.

In order to check the above data for heats of mixing, we measured the heats of solution of the complex salt $[Ni(NH_3)_6]Cl_2$. A direct relation exists between the heat of solution of $[Ni(NH_3)_6]Cl_2$ and the heat of mixing of $NiCl_2$ solution with ammonia solution.

We may write the equations of the two processes as follows:

$$NiCl_2\,aq. + 6NH_3\,aq.' = [Ni(NH_3)_6]Cl_2\,aq.'', \qquad (II)$$

$$[Ni(NH_3)_6]Cl_2 \text{ solid} + aq.' = [Ni(NH_3)_6]Cl_2 \text{ aq.}', \quad \text{(III)}$$

where aq' is aqueous ammonia solution.

Let L be the heat of solution of solid $[Ni(NH_3)_6]Cl_2$, and Q the thermal effect of reaction (II). From the thermochemical tables of Britske and Kapustinskii [8] we get the heats of formation of the substances participating in reactions (II) and (III), and we can then calculate the heat of formation of $[Ni(NH_3)_6]Cl_2$ aq' in both equations. For the first equation it is 239.1 + L; for the second it is 210.3 + Q. Equating these values we get:

$$239.1 + L = 210.3 + Q,$$

and hence:

$$Q - L = 28.8 \text{ kcal.} \quad (1)$$

We see from Table 4 that the heat-of-solution data are in agreement with the heat-of-mixing data.

TABLE 4

Relation Between Heat of Mixing and Heat of Solution

	Concentration (moles/liter)	Heat of solution of $[Ni(NH_3)_6]Cl_2$ L	Heat of mixing of $NiCl_2$ with ammonia solutions Q	Difference between	
				Heat of mixing and heat of solution Q − L	Heat of mixing and heat of solution as reported in the literature
1	0.70	−10.40	18.80	29.20	28.80
2	0.50	−11.92	17.80	29.72	—

Several theories have been advanced about the process of formation of the $Ni(NH_3)_6^{2+}$ ion, but the only one which accounts for the change in heat of mixing is that the formation of the ion proceeds according to the scheme:

$$[Ni(NH_3)_4]^{2+}_{aq.} + 2NH_3 \text{ aq} \rightleftharpoons [Ni(NH_3)_6]^{2+}_{aq.}.$$

We calculated the equilibrium constant of reaction (I) from the experimental heats of mixing.

Designating the equilibrium concentrations of $[Ni(NH_3)_6]^{2+}$, $[Ni(NH_3)_4^{2+}]$ and NH_3 respectively by a, b, and c, and bearing in mind that

$$\frac{a}{bc^2} = K, \quad (2)$$

we obtain the following expression for the heat of mixing:

$$Q = \frac{Kc^2}{Kc^2 + 1} \cdot 26 + \frac{1}{Kc^2 + 1} \cdot A, \quad (3)$$

where 26 is the heat of formation of the $[Ni(NH_3)_6]^{2+}$ ion and A is the heat of formation of the $[Ni(NH_3)_4]^{2+}$ ion (equal to 17 cal).

Following a series of rearrangements we obtain the following expression for the equilibrium constant of the above reaction:

$$K = \frac{Q - A}{(26 - Q)c^2}. \quad (4)$$

The values of the constant calculated with this formula appear in Table 5.

The mean value of this constant is 0.43. Using this value we calculated the heat of mixing. In the majority of cases the difference between the values obtained and the experimental ones was within the limits of possible experimental error. In some cases, however, it attained a very high value; hence we can only regard the value of the constant as an approximate one.

As a check on the obtained values of the equilibrium constant we determined the same constant by the solubility method. The solubility of the complex salt $[Ni(NH_3)_6]I_2$ in ammonia solutions of various concentrations was measured. With increasing ammonia concentration the solubility of this salt ought to have fallen with the decrease in degree of dissociation of the $[Ni(NH_3)_6]^{2+}$ ion. The solubility product of the complex salt $[Ni(NH_3)_6]I_2$ was calculated from the limiting solubility and was equal to $5.5 \cdot 10^{-6}$. With the help of this value we calculated the concentration of the $[Ni(NH_3)_6]^{2+}$ ion for all the investigated points. We considered the difference between the observed solubility and the calculated concentration of the $[Ni(NH_3)_6]^{2+}$ ion to be the concentration of the $[Ni(NH_3)_4]^{2+}$ ion. The following expression was obtained for the equilibrium constant of reaction (I):

$$K = \frac{SP}{4S^3\left(S - \frac{SP}{4S^2}\right)[NH_3]^2}, \quad (5)$$

where SP is the solubility product of $[Ni(NH_3)_6]I_2$, and S is the solubility of $[Ni(NH_3)_6]I_2$.

TABLE 5
Calculation of the Equilibrium Constants of Reaction (I) from the Thermochemical Data

	NH_3 conc. in moles/liter	Heat of mixing (in kcal)	Equilib. const. of (I)	Heat of mixing (in kcal) calculated from the mean value of the constant
1	0.47	17.78	0.43	17.79
2	0.65	18.76	0.57	18.36
3	0.95	19.65	0.46	19.44
4	1.17	20.06	0.38	20.30
5	1.28	20.44	0.37	20.66
6	2.46	22.80	0.30	23.46
7	3.60	23.94	0.27	24.61
8	4.65	25.04	0.39	25.11
9	5.21	25.48	0.59	25.27
10	6.24	25.50	0.43	25.48
	Mean value		0.43	–

The results of calculation of the constant are presented in Table 3.

Comparison of the constants calculated from the heats of mixing with those from solubility data shows that the values are of the same order although not identical. The deviations may be due to the inadequate accuracy of the calorimetric method. However, similar discrepancies occur in the determination of the stability constants by different methods [6].

The literature data for the stability constants of one and the same ion obtained even by the same method differ among themselves. Thus, for PbI_3^-, Korenman [7] gives a value of $0.93 \cdot 10^{-6}$ to $7.4 \cdot 10^{-6}$. Still wider deviations are found when comparing the data of other authors. On the basis of the equilibrium constants obtained by both methods we can conclude that two molecules of ammonia simultaneously join on to the $Ni(NH_3)_4^{2+}$ ion, and not one molecule as Bjerrum suggested [3].

We applied the obtained thermodynamic data to a series of calculations.

The standard heats of formation of the $[Ni(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ ions in solution were calculated, the values being $[Ni(NH_3)_4]^{2+}_{aq.}$. For the former $\Delta H^\circ_{298} = -109.6$ kcal; for the latter $\Delta H^\circ_{298} = -157.3$ kcal.

We calculated the change of free energy during formation of the complex ions of $[Ni(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ from the equation:

$$-\Delta Z = RT \ln K, \quad (6)$$

where K is the equilibrium constant of formation of the given ion.

The following values were obtained: For the reaction: $[Ni(NH_3)_4]^{2+}$ and $[Ni(NH_3)_2]^{2+}$

$$Ni^{2+}_{aq.} + 4NH_{3aq.} = [Ni(NH_3)_4]^{2+}_{aq.} \qquad \Delta Z = 10.5 \text{ kcal}$$

The equilibrium constant of this reaction was taken from Bjerrum's data [3].

For the reaction:

$$[Ni(NH_3)_4]^{2+}_{aq.} + 2NH_{3aq.} \rightleftharpoons [Ni(NH_3)_6]^{2+}_{aq.} \qquad \Delta Z = 0.13 \text{ kcal}$$

The equilibrium constant of the reaction was taken from our thermodynamic data.

From the heat-of-formation and the change-of-free-energy data we evaluated the entropies of the complex ions of $[Ni(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ in solution, the following values being obtained:

$$[Ni(NH_3)_4]^{2+}_{aq.} = 54.3$$

$$[Ni(NH_3)_6]^{2+}_{aq.} = 76.78.$$

Utilizing the heat-of-formation data for the solid salt $[Ni(NH_3)_6]I_2$ and the iodine ion [8], and knowing the heat of formation of the $[Ni(NH_3)_6]^{2+}_{aq.}$ ion, we determined the heat of solution of $[Ni(NH_3)_6]I_2$.

From the heat of solution and the solubility of $[Ni(NH_3)_6]I_2$ we calculated the entropy of solution of the solid salt $[Ni(NH_3)_6]I_2$ which was 2.7.

Knowing the entropy of the ions in solution and the entropy of solution, we calculated the entropy of the solid salt $[Ni(NH_3)_6]I_2$. It is approximately 130.1 cal/g.

SUMMARY

1. Determinations were made of the heats of mixing of $NiCl_2$ solutions with ammonia solutions of various concentrations, and calculations were made of the heats of formation of the $[Ni(NH_3)_6]^{2+}$ and $[Ni(NH_3)_4]^{2+}$ ions in aqueous solution.

2. The equilibrium constant of the reaction:

$$[Ni(NH_3)_4]^{2+}_{aq.} + 2NH_{3aq.} \rightleftharpoons [Ni(NH_3)_6]^{2+}_{aq.}$$

was determined from thermodynamic data and from data for the solubility of $[Ni(NH_3)_6]I_2$ in ammonia solutions. It was equal to $\underline{n} \cdot 10^{-1}$ ($\underline{n} = 4-9$).

3. The hypothesis is proposed that two molecules of ammonia add on simultaneously to the $[Ni(NH_3)_4]^{2+}$ ion.

4. Approximate calculations are made of the entropies of the $[Ni(NH_3)_6]^{2+}$ and $[Ni(NH_3)_4]^{2+}$ ions in solution, and also of the entropy of the solid salt $[Ni(NH_3)_6]I_2$.

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Received May 3, 1951

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* See Consultants Bureau translation, p. 2219.

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THE SOLUBILITY PRODUCT OF LEAD HYDROXIDE

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The solubility product of lead hydroxide, according to several publications [1-3], is $6.8 \cdot 10^{-13}$. This value is calculated from the solubility of $Pb(OH)_2$ on the assumption that in its saturated solution the electrolyte is completely dissociated. According to other sources [4] the solubility product of lead hydroxide is taken to be equal to $2.8 \cdot 10^{-16}$, but here also complete dissociation is assumed. It is impossible, however, to regard this assumption as justified, for it is known that lead hydroxide is a weak electrolyte. Its dissociation constants [5] are fairly low – $K_1 = 9.6 \cdot 10^{-4}$ and $K_2 = 3 \cdot 10^{-8}$. It can therefore be shown that lead hydroxide is only partly dissociated in saturated solution. Applying the solubility of this hydroxide and its dissociation constants, we have calculated the solubility product of $Pb(OH)_2$ and have obtained a value of $8.17 \cdot 10^{-17}$. Finally, the solubility product (SP) can be calculated if we know the pH of the lead salt solution at the start of formation of $Pb(OH)_2$:

$$[Pb^{\cdot\cdot}][OH^{-}]^2 = SP \text{ or } \frac{[Pb^{\cdot\cdot}]K^2_{H_2O}}{[H^{+}]^2} = SP$$

hence:

$$\log SP = \log[Pb^{\cdot\cdot}] + 2\log K_{H_2O} - 2\log[H^{+}] \text{ or } \log SP = \log[Pb^{\cdot\cdot}] - 2pK_{H_2O} + 2pH.$$

For the purpose, therefore, of calculating the solubility product we must know the pH at the start of precipitation of the hydroxide and the concentration of lead ions at that instant. We could not find accurate data on this problem in the literature. In the majority of papers the pH at the start of precipitation of the hydroxide is given without indication of the corresponding concentration of the lead salt, and only in one instance [6] is it noted that lead hydroxide begins to come down from 0.02 molar lead nitrate solution at an approximate pH of 6. On this basis calculation gives a value of $SP = 2 \cdot 10^{-18}$. It is understood that this value must likewise be considered approximate. These data show that the solubility product of $Pb(OH)_2$ must be considerably lower than the values given in the literature.

With the aim of more accurate determination of the solubility product of lead hydroxide we performed a series of investigations which involved determination of the pH of the solution at the instant of formation of the hydroxide, using solutions of various ionic strengths. The pH was determined potentiometrically with the help of a quinhydrone electrode accurate to $\pm$ 0.01 pH.

To 5 ml of lead nitrate solution of definite concentration was added, from a microburet, an 0.01 N solution of sodium hydroxide free from carbonate; the pH of the solution was measured after addition of each portion of alkali and mixing. As an example we give the results of a series of experiments with 0.05 M solution of lead nitrate (Table 1).

TABLE 1

Experiments with 5 ml of 0.05 M Lead Nitrate Solution at 22°

Volume of 0.01 N NaOH solution added (ml)	0	0.05	0.10	0.15	0.20	0.30	0.40	0.50
pH	4.59	4.66	4.82	4.94	5.03	5.09	5.10	5.11

A graph of pH of solution versus volume of alkali solution added was plotted from the data obtained. The start of precipitation of hydroxide is given by the point at which an inflection of the curve is observed; in the present case the pH at the start of precipitation was 5.03. The lead ion concentration at that instant was $\frac{0.05 \cdot 5}{5.20} = 0.048$ g-ion/l and $\log [Pb^{\cdot\cdot}] = \bar{2}.68$.

Consequently:

$$\log SP = \bar{2}.68 - 2 \cdot 14 + 2 \cdot 5.03 = \overline{20}.74.$$

Hence:

$$SP = 5.5 \cdot 10^{-20}.$$

We repeated these measurements with 0.05 M lead nitrate solutions containing various amounts of cadmium nitrate (Table 2), i.e., with solutions with identical lead ion concentrations but with various ionic strengths (μ).

For the determination of the solubility product, or, more correctly, the activity product* in saturated $Pb(OH)_2$ solution, it is necessary to find this magnitude at an ionic strength substantially equal to zero. The solubility of $Pb(OH)_2$ is so small that the ionic strength of a saturated solution is very close to zero. From the data of Table 2 we constructed a graph of the solubility product as a function of the ionic strength and we extrapolated to zero ionic strength. In this manner we find that the solubility product at zero ionic strength or the activity product is equal to $1.1 \cdot 10^{-20}$ ($-\log SP = 19.96$).

TABLE 2

Determination of Solubility Product of $Pb(OH)_2$ in Solutions of Various Ionic Strengths at 22°.

Initial concentration (M/l)		Concentration at start of precipitation (M/l)		μ	pH of solution at start of precipitation of $Pb(OH)_2$	Sp of lead hydroxide	$-\log SP$
$Pb(NO_3)_2$	KNO_3	$Pb(NO_3)_2$	KNO_3				
0.05	0	0.048	0	0.144	5.03	$5.5 \cdot 10^{-20}$	19.26
0.05	0.04	0.049	0.039	0.186	5.17	$1.05 \cdot 10^{-19}$	18.98
0.05	0.08	0.049	0.078	0.225	5.29	$1.82 \cdot 10^{-19}$	18.74
0.05	0.12	0.05	0.12	0.270	5.38	$2.81 \cdot 10^{-19}$	18.56
0.05	0.18	0.05	0.18	0.330	5.52	$5.49 \cdot 16^{-19}$	18.26

Similar measurements were made at 40° and 60° (Table 3).

TABLE 3

Determination of Solubility Product of Lead Hydroxide at 40 and 60°

Conc. at start of precipitation (M/l)		μ	pH of solution at start of precipitation	SP of lead hydroxide	$-\log SP$	Note
$Pb(NO_3)_2$	KNO_3					
0.048	0	0.144	4.76	$2.3 \cdot 10^{-19}$	18.64	40°
0.048	0.039	0.183	4.82	$3.1 \cdot 10^{-19}$	18.51	$I^{40}_{H_2O} = 10^{-13.42}$
0.048	0.078	0.222	5.00	$6.9 \cdot 10^{-19}$	18.16	
0.048	0.118	0.262	5.13	$1.26 \cdot 10^{-18}$	17.90	
0.049	0.176	0.323	5.31	$2.92 \cdot 10^{-18}$	17.51	
0.048	0	0.144	4.24	$2.3 \cdot 10^{-19}$	18.64	60°
0.048	0.039	0.183	4.32	$3.39 \cdot 10^{-19}$	18.47	$I^{60}_{H_2O} = 10^{-12.9}$
0.049	0.078	0.225	4.61	$1.29 \cdot 10^{-18}$	17.89	
0.049	0.116	0.263	4.70	$1.90 \cdot 10^{-18}$	17.72	
0.049	0.175	0.322	4.82	$3.31 \cdot 10^{-18}$	17.48	

Graphical extrapolation to zero ionic strength leads to the following values of the activity product of lead hydroxide:

at 22° . . . $1.1 \cdot 10^{-20}$,
at 40° . . . $3.2 \cdot 10^{-20}$,
at 60° . . . $3.5 \cdot 10^{-20}$.

SUMMARY

1. The activity products of lead hydroxide were determined at 22, 40 and 60°. It was shown that these values slightly increase with rising temperature.

2. The activity product of lead hydroxide at 22-60° is $1.1-3\ 5 \cdot 10^{-20}$.

3. The change of ionic strength of the solution has a considerable influence upon the solubility product

* $[Pb^{\cdot\cdot}][OH']^2 f_{Pb^{\cdot\cdot}} f^2_{OH'} = P_a$ or $SP f_{Pb^{\cdot\cdot}} f^2_{OH'} = P_a$, where P_a is the activity product, a constant magnitude at the given temperature; SP is the solubility product, a magnitude depending on the temperature and the ionic strength of the solution; f is the activity coefficient.

of lead hydroxide; this effect is intensified with rising temperature.

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Received March 7, 1951

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PHYSICO-CHEMICAL ANALYSIS OF SYSTEMS OF THE HALIDES OF MERCURY, THE ALKALI METALS AND AMMONIUM

III. ELECTRICAL CONDUCTIVITY OF THE SYSTEMS $HgHa_2$–NH_4Ha IN MELTS

I. N. Belyaev and K. E. Mironov

In Communications I and II, data were presented for the fusibility of the systems $HgHa_2$–MeHa*. In the present communication we give results of an investigation of the electric conductivity of the systems $HgHa_2$–NH_4Ha.

The investigation of the electric conductivity of fused salt systems helps to add precision to data for the existence and composition of complex compounds detected by the fusibility method.

It was shown by the researches of A. G. Bergman and co-workers, Tarasova and others [1,2,3] that compounds detected on the liquidus line of the fusion diagram are characterized by sharp minima on the isotherms of specific electric conductivity of the melts. These sharp minima are observed both in the case of congruently and incongruently melting compounds. Depending upon the difference in magnitudes of the specific conductivity of the fused components, the minima on the conductivity isotherms are shifted more or less from the axis of composition of the compound in the direction of the less-conductive component [3].

Up to the present not more than two minima have been observed [3,4] on the isotherms of specific electric conductivity of fused binary systems, and indications have been obtained of a third minimum [14].

From this aspect great interest is attached to a study of the very intriguing chemistry of the system $HgHa_2$–NH_4Ha.

EXPERIMENTAL

Electric conductivities were measured in the apparatus previously described by one of us [5]. The cell was a modified Biltz cell of pyrex. It comprises four parts (Fig. 1): a small pipet with capillary a holds the internal electrode introduced into a glass tube. The outer electrode in the tube b and the thermocouple t (nichrome-constantan) are hermetically joined to a at point c with the help of an insulating disc** which ensured constant distance between the electrodes and permitted accurate measurement of the temperature of the melt. The cap d forced the cell into the test tube precisely to the stop piece e, thus enabling the maintenance of constant distance between the capillary of the pipet and the bottom of the test tube.

The electrodes were platinized to enable a sharp minimum in the sound in the earphones to be detected [6].

The cell constant was established against 0.1 N and 0.01 N NaCl solutions at 25° [4]. No corrections were made for the temperature. During the investigation the cell constant was systematically checked after 20-30 determinations. The temperature was determined by the method described in the preceding communications.

The test tube containing the cell was placed in a molybdenum glass casing immersed in a porcelain beaker containing a eutectic melt with the composition (weight-%) 44.9% KNO_3; 43.8% $Ca(NO_3)_2$; 11.3% $NaNO_3$. This melted at 133° and permitted heating to 450° [7,8]. Heating was performed in an electrical resistance furnace.

The large bulk of the eutectic melt (up to 2.5 kg) permitted smooth and gradual fall of temperature at the rate of 2-3° per minute.

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* Me = Na, K, NH_4; Ha = Cl, Br, I.

** The temperature for the systems $HgBr_2$ and HgI_2 was measured in this way; in the case of $HgCl_2$–NH_4Cl the thermocouple was placed between the test tube and the casing.

Figure 1. Cell for measurment of electric conductivity. Details in text.

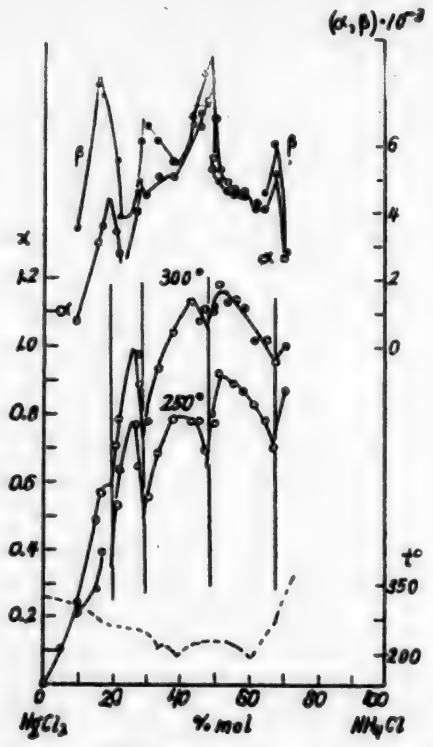

Figure 2. System $HgCl_2$–NH_4Cl. χ - specific electric conductivity; $\alpha \cdot 10^{-3}$ and $\beta \cdot 10^{-3}$ – its absolute and relative temperature coefficients.

The electric conductivities were measured polythermally and were extrapolated in some cases to 10-20°.

Isotherms through 25° were plotted from the polytherms.

On the basis of the isotherms the temperature coefficient of the specific electric conductivity through 50° was determined

$$\left(\text{absolute } \alpha = \frac{\chi_2 - \chi_1}{t_2 - t_1} \text{ and relative } \beta = \frac{\chi_2 - \chi_1}{t_2 - t_1} \cdot \frac{1}{\chi_{av.}}\right).$$

This added precision to the data for the existence of compounds [9, 10].

Agreement of a series of repeated measurements testified to the accuracy of the method.

The reagents used have been described before. The magnitudes of the specific electric conductivities of $HgCl_2$ and HgI_2 agreed with the handbook data [4]; we found for $HgBr_2$: $\chi_{235}^{\circ\circ} = 1.7 \cdot 10^{-4}$ ohm^{-1} cm^{-1}, instead of $\chi_{235}^{\circ} = 14.5 \cdot 10^{-4}$ ohm^{-1} cm^{-1}; according to Biltz the melting point is 243° instead of 238° [11]. The lower specific electric conductivity and the higher melting point reflect the high purity of our preparation.

System $HgCl_2$ – NH_4Cl

The fusibility of the system has been examined previously. The liquidus line has transition points at 243, 235, 214° with respective contents of 18.5, 23.5 and 33.5 mole-% NH_4Cl, corresponding to the compounds $9HgCl_2 \cdot NH_4Cl$; $3HgCl_2 \cdot NH_4Cl$; and $2HgCl_2 \cdot NH_4Cl$. The compound $HgCl_2 \cdot NH_4Cl$ is characterized by a flat maximum at 218° and 50 mole-%•• NH_4Cl. The transition point of 243° and 66.6% NH_4Cl correspond to the compound $HgCl_2 \cdot 2NH_4Cl$.

The specific electric conductivity of the system was studied in the range 225-300°. The 225, 250, 275 and 300° isotherms were constructed from the data of 25 polytherms (Fig. 2, Table 1). Four minima appear on the specific conductivity isotherms, two of which are sharp at 30 and 49% NH_4Cl and correspond to the compounds $2HgCl_2 \cdot NH_4Cl$ and $HgCl_2 \cdot NH_4Cl$. These minima are reflected by sharp maxima on the curves of the temperature coefficients of the electric conductivity.

The third minimum, corresponding to the 9:2 compound, is not sharply developed on the conductivity isotherms but is represented by a sharp maximum on the temperature coefficient curves.

The position of the fourth minimum, on the conductivity isotherms corresponding to $HgCl_2 \cdot 2NH_4Cl$, was

•

•• Data extrapolated to 15°.
Mole-percentages are given throughout.

TABLE 1

Specific Electric Conductivity of the System $HgCl_2$–NH_4Cl

Expt. No.	NH_4Cl (%)	x				$\alpha \cdot 10^3$	$\beta \cdot 10^3$
		225°	250°	275°	300°	250-300°	250-300°
1	0.0	–	–	–	0.000124	–	–
2	5.1	–	–	0.090	0.111	–	–
3	10.0	–	0.219	0.231	0.242	0.82	3.52
4	15.9	–	0.284	0.383	0.491	3.12	7.80
5	17.0	–	0.394	0.486	0.577	3.64	7.47
6	21.5	–	0.537	0.625	0.711	3.47	5.55
7	22.0	–	0.648	0.718	0.790	2.80	3.90
8	27.0	0.657	0.779	0.889	0.985	4.11	4.62
9	28.0	0.504	0.650	0.786	0.891	4.81	6.11
10	30.0	0.432	0.561	0.682	0.787	4.52	6.63
11	33.4	0.547	0.688	0.817	0.940	5.05	6.18
12	37.6	0.616	0.790	0.930	1.048	5.13	5.52
13	43.2	0.602	0.787	0.970	1.131	6.62	6.81
14	45.2	0.618	0.784	0.940	1.075	6.59	6.93
15	47.3	0.458	0.700	0.923	1.116	7.30	8.10
16	49.7	0.591	0.802	0.976	1.111	6.78	6.78
17	50.0	0.730	0.785	1.080	1.122	5.68	5.33
18	51.5	0.707	0.928	1.077	1.183	5.27	4.91
19	53.8	–	–	1.046	1.138	4.88	4.63
20	55.8	0.702	0.890	1.040	1.137	4.73	4.56
21	58.2	0.707	0.378	1.023	1.113	4.60	4.52
22	62.0	0.678	0.838	0.953	1.023	4.16	4.34
23	65.0	0.630	0.790	0.925	1.021	4.16	4.57
24	67.8	–	0.702	0.855	0.960	5.17	6.04
25	70.6	–	0.877	0.948	1.010	2.62	2.76

determined approximately since the high content of NH_4Cl prevented measurement of the electric conductivity.

The minima on the conductivity isotherms at 30 and 49% NH_4Cl are shifted from the axis of the abscissas in the direction of the less conductive component, $HgCl_2$, to the extent of 1-4%, in agreement with the literature data [3].

The displacement of the conductivity minima at 20 and 67.5% NH_4Cl from the abscissas in the direction of NH_4Cl and the scatter of the points in the 50-55% NH_4Cl region on the 300° isotherm are bound up with the fugacity of the components.

System $HgBr_2$–NH_4Br

Data for the fusibility of the system were presented in Communication II. On the liquidus line the following compounds were detected: $9HgBr_2 \cdot 2NH_4Br$; $3HgBr_2 \cdot 2NH_4Br$; $HgBr_2 \cdot NH_4Br$; and $HgBr_2 \cdot 2NH_4Br$, to which correspond the transition points at 222, 165, 201 and 266°, and the respective NH_4Br contents of 24.0, 40.0, 60.5 and 67.0%. The specific electric conductivity of the system was studied from 200 to 375°. The data from 33 polytherms were applied in plotting eight specific

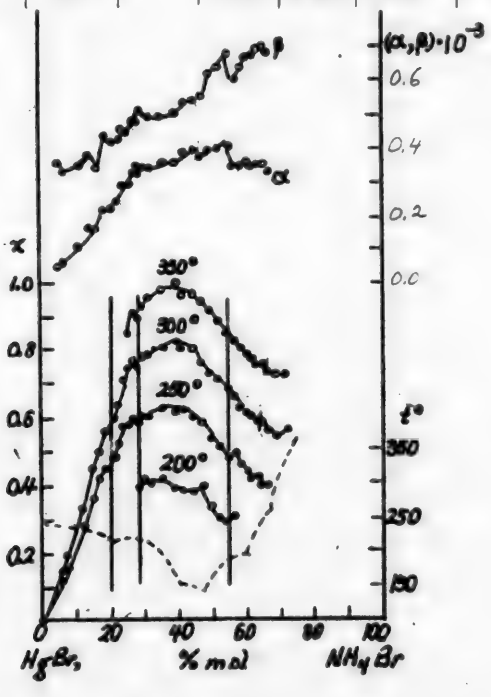

Fig. 3. System $HgBr_2$–NH_4Br. x – specific electric conductivity; $\alpha \cdot 10^{-3}$ and $\beta \cdot 10^{-3}$ are its absolute and relative coefficients.

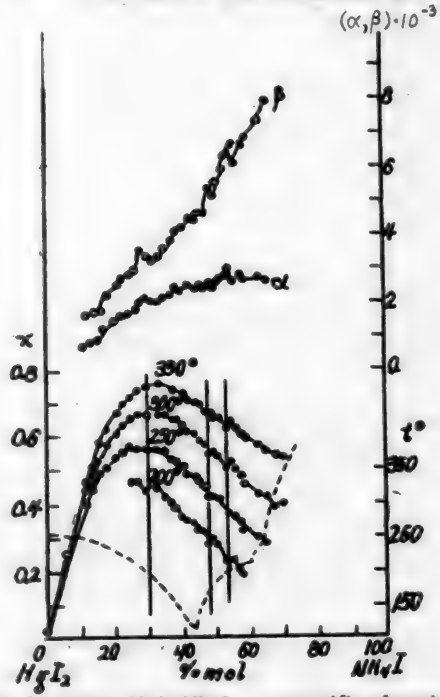

Fig. 4. System HgI_2–NH_4I. x – specific electric conductivity; $\alpha \cdot 10^{-3}$ – absolute coefficient; $\beta \cdot 10^{-3}$ – relative coefficient

TABLE 2

Specific Electric Conductivity of the System $HgBr_2$–NH_4Br

Prep. No.	NH_4Br	x								$\alpha \cdot 10^3$	$\beta \cdot 10^3$
		200°	225°	250°	275°	300°	325°	350°	375°	250-300°	250-300°
1	0	–	–	$0.026 \cdot 10^2$	0.042	0.078	–	–	–	–	–
2	6.0	–	–	0.128	0.140	0.151	–	–	–	0.50	3.57
3	7.5	–	–	0.163	0.180	0.194	–	–	–	0.60	3.33
4	12.0	–	–	0.287	0.320	0.340	–	–	–	1.12	3.50
5	15.0	–	0.315	0.368	0.417	0.455	–	–	–	1.60	3.84
6	17.0	–	0.378	0.425	0.469	0.503	–	–	–	1.62	3.46
7	19.0	–	0.400	0.454	0.510	0.565	0.618	–	–	2.23	4.37
8	21.1	–	0.425	0.486	0.545	0.602	0.655	–	–	2.30	4.22
9	22.5	–	0.451	0.522	0.586	0.642	0.691	–	–	2.49	4.24
10	24.0	–	0.485	0.568	0.645	0.712	0.770	–	–	2.90	4.53
11	26.0	–	0.498	0.583	0.665	0.743	0.805	0.845	–	3.00	4.50
12	27.5	–	0.520	0.600	0.682	0.763	0.832	0.910	–	3.28	4.81
13	28.5	–	0.500	0.587	0.672	0.751	0.829	0.897	–	3.26	4.85
14	29.0	0.395	0.493	0.590	0.681	0.767	0.837	0.902	–	3.50	5.12
15	30.0	0.424	0.517	0.607	0.693	0.778	0.858	0.930	–	3.43	4.95
16	32.0	0.412	0.518	0.610	0.699	0.786	0.872	0.958	–	3.46	4.95
17	36.0	0.426	0.534	0.629	0.718	0.805	0.891	0.978	–	3.59	5.00
18	40.0	0.398	0.517	0.621	0.723	0.824	0.917	1.003	–	3.62	5.01
19	42.0	0.394	0.510	0.623	0.717	0.805	0.883	0.963	–	3.84	5.33
20	45.0	0.385	0.503	0.607	0.713	0.804	0.887	0.965	–	3.90	5.45
21	47.5	0.395	0.498	0.588	0.680	0.766	0.856	0.943	–	3.80	5.58
22	50.0	0.336	0.436	0.542	0.638	0.734	0.828	0.914	–	3.92	6.27
23	52.5	0.307	0.412	0.517	0.623	0.716	0.805	0.887	–	4.03	6.47
24	55.0	0.297	0.390	0.488	0.582	0.682	0.768	0.852	–	4.02	6.85
25	57.0	0.317	0.404	0.492	0.578	0.666	0.745	0.822	–	3.50	6.06
26	59.0	–	0.383	0.461	0.548	0.636	0.723	0.805	–	3.52	6.41
27	60.5	–	0.352	0.440	0.528	0.619	0.704	0.786	0.874	3.60	6.73
28	62.0	–	0.339	0.428	0.516	0.603	0.688	0.772	0.859	3.54	6.80
29	64.0	–	0.334	0.421	0.507	0.594	0.676	0.759	0.842	3.54	6.99
30	65.0	–	0.305	0.402	0.497	0.594	0.685	0.760	0.825	3.53	7.08
31	67.0	–	–	0.402	0.484	0.566	0.647	0.731	0.814	3.32	6.87
32	69.0	–	–	–	–	0.552	0.638	0.727	0.818	–	–
33	72.0	–	–	–	–	0.569	0.648	0.726	0.807	–	–

electric conductivity isotherms for 200, 225, 250, 275, 300, 325, 350 and 375° (Fig. 3, Table 2). Two sharp minima were detected on the isotherms at 30 and 55% NH_4Br. The minimum at 55% NH_4Br corresponds to the 1:2 compound. This minimum flattens out with rising temperature and is no longer visible on the 300° isotherm.

The minimum at 30% NH_4Br on the liquidus curve does not correspond to any compound, but its existence and the fact that it persists on all the isotherms suggest that a 2:1 compound is present in the melt. The slight inflection of the liquidus line in this region of concentrations is regarded as due to experimental error.

In addition to the described minima, an inflection is observed on the electric conductivity isotherms corresponding to the 9:2 compound which is fairly clearly characterized on the liquidus line. The reflection of this compound on the conductivity isotherms by an inflection and not by a minimum is probably due to the sharp rise in conductivity in the narrow range of concentration.

Sharp maxima on the temperature coefficient curves of the specific conductivity correspond to the minima on the conductivity isotherms. The turning point on the conductivity isotherm corresponds to a small sharp maximum on the temperature coefficient curves.

TABLE 3

Specific Electric Conductivity of the System $HgBr_2$–NH_4Br

Expt. No.	NH_4I %	x							$\alpha \cdot 10^3$	$\beta \cdot 10^3$
		200°	225°	250°	275°	300°	325°	350°	250-300°	250-300°
1	0.0	–	–	–	0.0310	0.0285	0.0275	0.0260	–	–
2	6.0	–	–	–	0.259	0.263	0.267	0.270	–	–
3	12.0	–	–	0.407	0.428	0.442	0.456	0.465	0.72	1.68
4	14.0	–	–	0.442	0.467	0.484	0.500	0.514	0.84	1.79
5	16.0	–	–	0.487	0.516	0.535	0.559	0.578	0.94	1.83
6	18.0	–	–	0.510	0.543	0.573	0.598	0.623	1.24	2.28
7	21.0	–	0.494	0.538	0.578	0.613	0.646	0.672	1.48	2.56
8	22.5	–	0.500	0.552	0.594	0.633	0.668	0.695	1.63	2.75
9	25.0	0.464	0.518	0.567	0.611	0.653	0.690	0.720	1.73	2.84
10	27.0	0.453	0.514	0.566	0.615	0.661	0.700	0.736	1.86	3.02
11	28.5	0.449	0.511	0.566	0.618	0.667	0.711	0.748	2.07	3.51
12	30.0	0.443	0.507	0.564	0.618	0.667	0.712	0.751	2.13	3.40
13	31.5	0.453	0.512	0.567	0.622	0.668	0.714	0.753	2.03	3.26
14	33.0	0.446	0.506	0.567	0.616	0.668	0.725	0.756	2.07	3.36
15	35.0	0.422	0.487	0.552	0.613	0.663	0.713	0.754	2.21	3.61
16	37.0	0.408	0.474	0.535	0.593	0.650	0.702	0.747	2.30	3.88
17	38.5	0.390	0.458	0.523	0.588	0.647	0.702	0.740	2.44	4.15
18	40.0	0.367	0.442	0.512	0.577	0.636	0.687	0.727	2.42	4.21
19	42.5	0.353	0.422	0.490	0.555	0.616	0.673	0.715	2.52	4.49
20	44.0	0.348	0.416	0.480	0.544	0.604	0.660	0.704	2.44	4.49
21	45.0	0.327	0.400	0.466	0.530	0.592	0.643	0.691	2.50	4.62
22	46.5	0.323	0.392	0.457	0.519	0.578	0.635	0.680	2.43	4.62
23	48.0	0.280	0.358	0.424	0.493	0.555	0.613	0.669	2.62	5.33
24	49.0	0.298	0.362	0.426	0.490	0.551	0.611	0.661	2.50	5.10
25	50.5	0.275	0.348	0.415	0.484	0.546	0.602	0.652	2.66	5.51
26	52.0	0.258	0.324	0.394	0.463	0.528	0.592	0.648	2.75	5.94
27	53.0	0.240	0.305	0.372	0.443	0.510	0.572	0.628	2.80	6.31
28	54.0	0.224	0.298	0.372	0.449	0.524	0.588	0.640	3.00	6.67
29	55.5	0.236	0.302	0.365	0.432	0.502	0.563	0.620	2.62	6.12
30	57.5	0.208	0.281	0.348	0.420	0.488	0.553	0.607	2.79	6.65
31	58.0	0.194	0.260	0.328	0.398	0.465	0.533	0.601	2.73	6.83
32	62.5	–	–	0.304	0.368	0.437	0.505	0.575	2.70	7.36
33	65.0	–	–	0.283	0.355	0.424	0.493	0.557	2.63	7.98
34	67.5	–	–	0.248	0.324	0.398	0.470	0.543	–	–
35	70.0	–	–	0.276	0.339	0.402	0.468	0.534	–	–

From the character of the conductivity isotherms (particularly the 300° isotherm) we may expect a minimum corresponding to the compound $HgBr_2 \cdot 4NH_4Br$.

It was not possible to establish its position accurately because of the very small difference in melting and boiling points of mixtures of this composition.

System HgI_2–NH_4I

The liquidus lines in this system pointed to the existence of two incongruently melting compounds, $HgI_2 \cdot 2NH_4I$ and $HgI_2 \cdot 4NH_4I$, with transition points at 210 and 234° and with NH_4I contents of ,respectively, 60 and 63%.

The electric conductivity of the system was studied by the plotting of 35 polytherms from which were prepared seven specific conductivity isotherms for 200, 225, 250, 275, 300, 325 and 350° (Fig. 4 and Table 3). The 200° isotherm contains three sharp minima at 30, 48 and 53% NH_4I, only one of which (53%) corresponds to

a chemical compound detected on the liquidus line during investigation of the fusibility. The two other minima at 30 and 48% NH_4I are not reflected by any inflections on the liquidus curve, but their presence on the conductivity isotherms points to the occurrence of chemical reaction in the melts. Compounds are here possibly formed with the composition $2HgI_2 \cdot NH_4I$ and $HgI_2 \cdot NH_4I$. Both of these minima flatten out with rising temperature and are no longer present on the 350° isotherm. All the minima on the conductivity isotherms of the system are reflected by sharp maxima on the temperature coefficient curves.

In the concentration region corresponding to the compound $HgI_2 \cdot 4NH_4I$, indicated on the liquidus line in the form of a crystallization branch between 210 and 234°, the electric conductivity was not investigated due to the very small melting point and boiling point differences of the mixtures close to the composition of this compound. Judging, however, by the character of the 250 and 300° isotherms in the region of 65-70% NH_4I, a minimum on the conductivity isotherms corresponding to this compound can be expected.

The first conspicuous feature observed on comparing the specific conductivity data of the above systems is the trend of change in the general character of the conductivity isotherms in the series Cl–Br–I. In the system $HgCl_2$–NH_4Cl the isotherms have a general rise from $HgCl_2$ to NH_4Cl, the values of the minima of the specific electric conductivity rise with the NH_4Cl concentration. In the system $HgBr_2$–NH_4Br a general rise of the isotherms is only observed up to 45% NH_4Br, after which the isotherms are bent toward the composition abscissas. In this region the values of the electric conductivity are lower at the minima than the values at the minima at the region of general rise of the isotherms. The fall in conductivity and the larger inclination of the isotherms to the composition abscissas starting from the general maximum is even more marked in the system HgI_2–NH_4I with rise of MeHa concentration.

The above-mentioned change in the general character of the conductivity isotherms in the series Cl–Br–I is closely associated with the fall in conductivity of MeHa in this series [4] and with the increased tendency to form compounds richer in NH_4 in the order Cl, Br, I; this leads to nonuniform change of conductivity of the resultant complex ions in the systems $HgHa_2$–NH_4Ha. Whereas in the system $HgCl_2$–NH_4Cl the conductivity of the formed complex ions increased with falling $HgCl_2$ content, in the system HgI_2–NH_4I the conductivity of the formed ions, starting from the general maximum on the conductivity isotherms (25%), should decrease with rising NH_4I content of the complex.

The character of the minima on the conductivity isotherms and of the maxima on the temperature coefficient curves is very clear-cut in the system $HgCl_2$–NH_4Cl, and the decreasing sharpness in the order Br, I confirms the previous conclusion about the increased susceptibility to complex formation and the increased stability of the complexes in the order I, Br, Cl with one and the same cation of alkali metal or ammonium.

Not more than two sharp minima on the conductivity isotherms have hitherto been detected [4,13] in studies of the electric conductivity of binary salt systems in melts, and there have been indications of a third one [12]. In the present investigation we succeeded in obtaining four sharp minima on the specific electric conductivity isotherms and the corresponding maxima on the temperature coefficient curves.

In the system $HgCl_2$–NH_4Cl in the low-concentration region, Foote and Martin [14] indicate the possibility of existence only of the complex $HgCl_2 \cdot NH_4Cl$. Our data for fusibility and electric conductivity indicate the existence of complexes richer in $HgCl_2$.

The most stable type of complex in a melt is $2HgHa_2 \cdot MeHa$, which is observed in all cases even when it does not appear on the liquidus line.

SUMMARY

1. The specific electric conductivity of the systems $HgCl_2$–NH_4Cl, $HgBr_2$–NH_4Br and HgI_2–NH_4I in melts has been investigated.

2. The electric conductivity method has confirmed that in melts the susceptibility to formation of complexes between $HgHa_2$ and MeHa increases in the order I, Br, Cl. The stability of the formed complexes also increases in that order.

3. For the first time isotherms of the specific electric conductivity of binary salt systems in melts have been obtained with four minima. On the temperature coefficient curves these minima are reflected by corresponding sharp maxima.

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Received March 2, 1951

Rostov-on-Don Molotov State University
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HIGHER MOLECULAR COMPOUNDS IN THE SYSTEM $CdCl_2$–KCl–H_2O

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In previous researches one of us showed [1] that by applying N. S. Kurnakov's principle of physicochemical analysis we can use refractometric data to establish the possible formation and to determine the molecular composition of higher molecular compounds in salt mixtures.

Among the physicochemical methods(utilizing heats of mixing, depression, electric conductivity, density, etc.) used for establishing the existence of molecular compounds in solutions, refractometry is one of the most accurate and convenient methods; on the basis of deviations from additivity of the refractive indices we can draw conclusions about the amount and form of molecular compounds formed in a solution of a given salt mixture.

Measurement of the refractive indices of salt mixtures (or measurement of any other physical constant) and comparison of the values with those theoretically calculated from the additivity law enables us, from the additivity deviation Δ_n, to infer the formation of higher molecular compounds from the components of the salt mixture. The composition of the chemical compound corresponds to a maximum or minimum on the curve of Δ_n versus composition of the mixture.

On the basis of the additivity law it is easy to calculate the theoretical value of the refractive index of a mixture (n-theoretical) from the usual formula:

$$\frac{a \cdot n_a + \beta n_\beta}{a + \beta} = n_{\text{theor.}},$$

where a = weight in grams of initial solution of one salt;
n_a = refractive index of the same starting solution;
β = weight in grams of starting solution of the second salt;
n_β = refractive index of the initial solution of the second salt.

The number of maxima or minima on the additivity deviation curve (Δ_n) permits an evaluation of the number of different forms of molecular compounds formed in a solution of the given salt mixture.

By applying certain optical methods, for instance photocolorimetry, it is believed [2] that the one most stable form of higher molecular compound can be detected, although for a given pair of salts several forms of molecular compounds may be formed in solution, as established by other physicochemical methods.

On the other hand, Babko [5] made extensive use of optical methods and of photometry in particular (change of extinction of solutions, measurement of the absorption spectra of complex groups) for determination of the dissociation constants (bond energies) and of the composition of complex compounds.

Vosburgh and Cooper [3], at first theoretically and later experimentally, showed that not one but several possible forms of higher compounds could be identified by the method of light absorption using a light filter to cut out all but a specific wave-length region.

As a check on the validity of the method we have carried out a refractometric study of the possibility of formation of molecular compounds in the system $CdCl_2$–KCl–H_2O, in which the first component (Cd^{++}) is a good complex-former known to yield not only ordinary higher molecular compounds with halogen addenda such as $M[CdHa_3]$ to $M_4[CdHa_6]$, but also autocomplexes of the type of $Cd[CdI_3]_2$, where M = metal.

EXPERIMENTAL

The starting solutions were prepared from chemically pure (guaranteed) $CdCl_2$ and KCl by solution of the calculated amount of salt in a weighed amount of water to give the required molar concentrations.

The salt content of the solution was later checked by titration.

Mixtures were prepared from the starting solutions by adding to a previously calculated and weighed amount of the solution of one component a calculated and weighed amount of solution of the second.

In this manner we avoid the errors admitted by Spacu and Popper [4] when they prepared the starting solutions by weight but prepared the salt mixtures by volume without considering that the weighed amounts are not volumetrically equivalent, and thus arrived at erroneous conclusions about the forms of the molecular compounds.

Since the weights of both of the starting materials are known, then from determinations of each of their indices of refraction we can calculate (on the basis of the additivity law) the theoretical values of the refractive indices ($n_{theor.}$) from the above formula.

Hence for each mixture we find the difference:

$$\Delta_n = n_{theor.} - n_{exp.}$$

If we now plot on the abscissas the composition of the mixture and along the ordinates the correspondingly determined deviations from additivity of the refractive indices (Δ_n); then we obtain a graph in which the maxima or the minima of the deviations from additivity correspond to the higher molecular compounds whose composition we find at the point on the abscissa opposite to the maximum or minimum on the curve of Δ_n versus composition of mixture.

As previously [1], the refractive indices were measured with the help of a Pulfrich immersion refractometer. The determinations were accurate to $\pm$ 0.05 scale divisions, corresponding to $\pm$ 1.82 units in the fifth place of the refractive index.

In the determinations of the refractive indices of the solutions use was made of three interchangeable prisms of the refractometer which served to cover the whole range of the change of refractive indices of the solutions of our salt mixtures:

1) prism 1 – n_D from 1.3254 to 1.3664,
2) " 2-L – n_D " 1.3642 to 1.3990,
3) " 3-L – n_D " 1.3989 to 1.4360.

Prism 1 was checked against distilled water, the two others with the help of special plates.

Concordant data were obtained by carefully adjusting the refractometer for each set of prisms.

During the refractometric determinations the temperature of the solutions was kept constant at 20°C $\pm$0.02° with the help of an ultrathermostat. Measurements were performed under conditions excluding evaporation of the solvent.

Data are presented in Tables 1 and 2 and in the diagram.

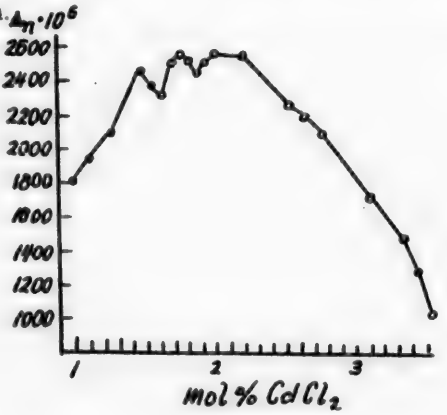
TABLE 1

System $CdCl_2$–KCl–H_2O (Starting Solutions)

Name	Mole-%	Molarity per 1000 g	Molecular weight	n_D^{20}
$CdCl_2$	4.4264	1.7473	183.324	1.392379
KCl	4.4215	2.1552	74.553	1.354898

In the system $CdCl_2$–KCl–H_2O the deviations from additivity of the refractive indices differ fundamentally from those observed by us for ternary systems [1] where the complex-formers were ions of alkali earth metals and magnesium. For the systems

$MgCl_2$–KCl–H_2O,
$SrBr_2$–NH_4Cl–H_2O,
$BaCl_2$–KCl–H_2O



System $CdCl_2$ – KCl – H_2O.

TABLE 2

Mixtures of Solutions of $CdCl_2$ and KCl

Expt. No.	Mole-% $CdCl_2$	Mole-% KCl	Mole-% Total	Mole-% H_2O	$n^{20}_{theor.}$	$n^{20}_{exp.}$	$\Delta\eta$ 10^6	$CdCl_2$/KCl
1	0.9833	3.4422	4.4255	95.5745	1.364672	1.362859	1813	1:3.5
2	1.1069	3.3198	4.4267	95.5733	1.365822	1.363881	1941	1:3
3	1.2656	3.1598	4.4254	95.5746	1.367295	1.365200	2095	1:2.5
4	1.4755	2.9510	4.4265	95.5735	1.369205	1.366760	2445	1:2
5	1.5603	2.8605	4.4208	95.5692	1.369976	1.367613	2363	1:1.83
6	1.6462	2.7811	4.4273	95.5727	1.370790	1.368476	2314	1:1.75
7	1.7069	2.7133	4.4202	95.5798	1.371286	1.368799	2487	1:1.59
8	1.7710	2.6515	4.4225	95.5775	1.371821	1.369292	2529	1:1.5
9	1.8272	2.5961	4.4233	95.5767	1.372320	1.369812	2508	1:1.42
10	1.8801	2.5402	4.4203	95.5797	1.372791	1.370356	2435	1:1.35
11	1.9444	2.4801	4.4205	95.5795	1.373350	1.370862	2488	1:1.22
12	2.0172	2.4114	4.4286	95.5714	1.373903	1.371366	2537	1:1.2
13	2.2102	2.2102	4.4204	95.5796	1.375607	1.373080	2527	1:1
14	2.5417	1.8813	4.4230	95.5770	1.378314	1.376076	2238	1.35:1
15	2.6546	1.7723	4.4269	95.5731	1.379269	1.377093	2176	1.5:1
16	2.7756	1.6484	4.4240	95.5760	1.380216	1.378149	2067	1.75:1
17	3.1608	1.2670	4.4278	95.5722	1.383192	1.381502	1690	2.5:1
18	3.3207	1.1068	4.4275	95.5725	1.384410	1.382962	1448	3:1
19	3.4430	0.9827	4.4257	95.5743	1.385328	1.384063	1265	3.5:1
20	3.5421	0.8854	4.4275	95.5726	1.386068	1.385052	1016	4:1

we always observed only one maximum, corresponding to the 1:1 composition, on the Δ_η/composition plot.

In the present case (Table 2 and diagram) the $\Delta\eta$/composition plot exhibits deviation from additivity represented by three maxima to which correspond mixtures of salts in the respective molar ratios of 1:1, 1:1.5 and 1:2.

Consequently in the case of the ternary system $CdCl_2$–KCl–H_2O we have detected molecular compounds with the compositions:

$1CdCl_2$: 1KCl, which corresponds to the composition $K[CdCl_3]$,
$1CdCl_2$: 1.5KCl, " " " " $2CdCl_2 \cdot 3KCl$,
$1CdCl_2$: 2KCl, " " " " $K_2[CdCl_4]$.

Spacu and Popper [4] also studied higher molecular compound formation in this system on the basis of refractive index changes in the mixtures, but they applied Job's [2] principle of continuous changes for the calculations, apart from which (as noted above) they prepared their starting solutions by weight and the mixtures by volume so that the results were confused by the nonequivalence between the gravimetric and volumetric data as well as by the differing densities of the starting solutions.

For the system $CdCl_2$–KCl–H_2O they claimed the formation of compounds not entirely identical with ours.

They obtained the following compounds:

$CdCl_2$: KCl = 1:1, corresponding to the composition $K[CdCl_3]$,
$CdCl_2$: KCl = 1:2, " " " $K_2[CdCl_4]$,
$CdCl_2$: KCl = 1:3, " " " $K_3[CdCl_5]$.

In view of the inaccuracy admitted by Spacu and Popper we made a recalculation of their data for the expression of the molarity of their solutions per 1000 g; the following values were obtained (Tables 3,4 and 5).

SUMMARY

The system $CdCl_2$–KCl–H_2O was studied by the method of physico-chemical analysis by measurement of the refractive indices of the solutions with the aim of establishing the possibility of formation of higher molecular compounds in solution.

TABLE 3

Starting solutions

Name	Molecular weight	Molarity per 1000 g solution	d_4^{20}	n^{20}	Molarity recalculated per 1 liter of solution
$CdCl_2$	183.324	2.0041	1.43030	1.404044	2.8664
KCl	74.553	1.9918	1.09685	1.352904	2.1847

TABLE 4

Mixtures of Solutions of $CdCl_2$ and KCl (Data of Spacu and Popper)

$CdCl_2$ + KCl (cm^3)	C (%)	n^{20}	d_4^{20}	$R_{exp.}$	$R_{theor.}$	$\Delta n \cdot 10^5$	C_{CdCl_2} (%)	C_{KCl} (%)
12+ 8	29.34	1.38336	1.29739	0.117755	0.118262	50.7	25.61	6.64
11+ 9	28.31	1.380752	1.28074	0.118903	0.119534	63.1	23.99	7.39
10+10	27.25	1.378150	1.26044	0.120190	0.120910	72.0	22.23	8.14
9+11	26.16	1.375516	1.246852	0.121845	0.122465	62.0	20.44	8.87
8+12	25.04	1.372985	1.230526	0.123355	0.124168	83.0	18.57	9.58
7+13	23.88	1.370367	1.213630	0.125247	0.126109	86.2	16.61	10.28
6+14	22.70	1.367802	1.196640	0.127554	0.128274	72.0	14.56	10.97
5+15	21.48	1.365221	1.17922	0.129940	0.130750	81.0	12.42	11.65
4+16	20.24	1.362590	1.163080	0.132899	0.133619	72.0	10.18	12.31

TABLE 5

Mixtures of $CdCl_2$ and KCl

Mixture No.	$CdCl_2$ + KCl (cm^3)	$CdCl_2$:KCl (cm^3)	Formulas of higher order compounds according to Spacu and Popper	$CdCl_2$–KCl (in moles 10^{-2})	$CdCl_2$:KCl (in moles)	Formulas of higher order compounds after recalculation	$\Delta n \cdot 10^5$ on curve
1	12+ 8	1.5 :1		3.44+1.746	1.97:1		50.7
2	11+ 9	1.22:1		3.15+1.964	1.61:1		63.1
3	10+10	1:1	$CdCl_2$:KCl	2.87+2.183	1.31:1	$\simeq CdCl_2$:KCl	72.0
4	9+11	1:1.22		2.58+2.40	1.07:1		62.0
5	8+12	1:1.5		2.29+2.62	1:1.14		83.0
6	7+13	1:1.86	$CdCl_2$:2KCl	2.01+2.836	1:1.41	$\simeq CdCl_2$:1.5KCl	86.2
7	6+14	1:2.33		1.72+3.055	1:1.77		72.0
8	5+15	1:3	$CdCl_2$:3KCl	1.43+3.274	1:2.29	$\simeq CdCl_2$:2KCl	81.0
9	4+16	1:4		1.147+3.49	1:3.04		72.0

1. The deviations from additivity of the refractive indices of solutions of salts in the system $CdCl_2$–KCl–H_2O demonstrated the existence of higher molecular compounds of the following compositions: $K[CdCl_3]$; $2CdCl_2 \cdot 3KCl$; $K_2[CdCl_4]$.

2. The refractometric method succeeded in showing the presence in solution of not only one but of several possible molecular compounds.

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Received May 28, 1951

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* See Consultants Bureau translation, p. 31.

DOUBLE DECOMPOSITION IN THE RECIPROCAL SYSTEM OF THE SULFATES AND TUNGSTATES OF SODIUM AND LEAD*

I. N. Belyaev

This investigation is one of a series on the study of complex formation and double decomposition in the reciprocal systems of the sulfates, molybdates and tungstates of sodium, potassium and lead in melts. The investigation was performed by the visual-polythermic method of physicochemical analysis described by many authors [1]. Mixtures of the salts were melted in a platinum crucible in a crucible resistance furnace, temperatures were measured with a platinum – platinum-rhodium thermocouple with a φ galvanometer, calibrated in the usual manner against the melting points of the chemically pure salts. The liquidus curves were plotted from the temperatures of appearance of the first crystals. For melts close to the invariant point the temperatures of complete setting were determined.

The following salts were used: Sodium sulfate, m.p. 884°; sodium tungstate, m.p. 695°; lead sulfate and tungstate prepared in the laboratory from dilute solutions of chemically pure, soluble salts of lead, sulfuric acid and sodium tungstate. Melts of the mixtures of the salts were perfectly transparent.

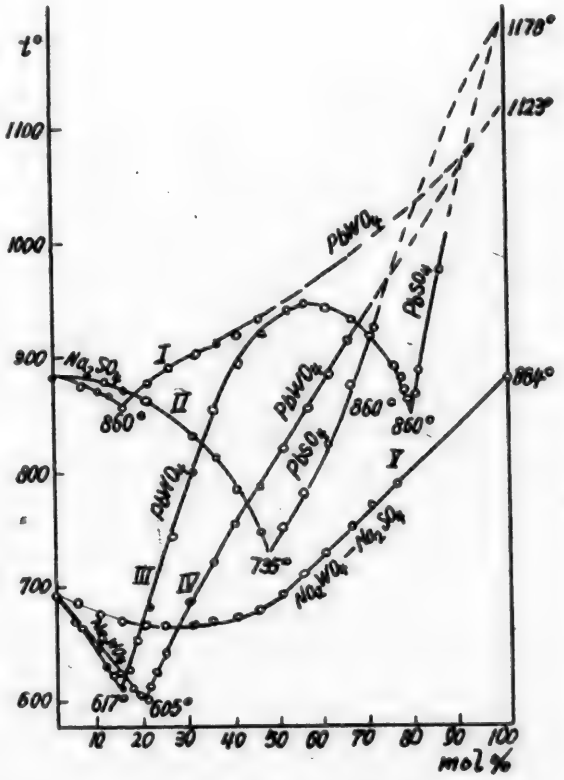

Fig. 1.

Sections: Na_2SO_4–$PbSO_4$ (II); Na_2WO_4–$PbWO_4$ (IV); Na_2WO_4–Na_2SO_4 (V); and diagonal sections: Na_2WO_4–$PbSO_4$ (III), Na_2SO_4–$PbWO_4$ (I).

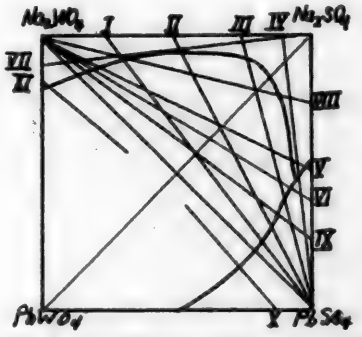

Fig. 2. Distribution of internal sections in the square of the reciprocal system

Sides: Three out of the four sides have been investigated by other authors [2]: Na_2SO_4–$PbSO_4$, Na_2SO_4–Na_2WO_4 and $PbSO_4$–$PbWO_4$. The first two of these have been repeated. The system Na_2SO_4–$PbSO_4$ has a simple eutectic at 735° and 47% $PbSO_4$ ** (Figures 1, II). The system Na_2WO_4–Na_2SO_4 (Table 1, Figure 1, V) comprises a continuous series of solid solutions with a minimum at, according to our measurements, 670° in the range of 20 to 40% Na_2SO_4 (Boeke gives [2] 633°). Limited reciprocal solubility is shown in the system $PbSO_4$–$PbWO_4$ with a eutectic at 995° and 50% $PbSO_4$. Our investigation of

* The investigation was carried out with the help of L. P. Nuzhnova.

** Molar percentages throughout.

TABLE 1

Fusibility of the System Na_2SO_4–Na_2WO_4

Expt. No.	Na_2WO_4 (%)	Temp. of appearance of first crystals	Solid phase
1	100	695	Na_2WO_4
2	95	688	
3	90	678	
4	85	672	
5	80	670	$Na_2 \parallel WO_4, SO_4$
6	75	670	
7	70	671	
8	65	672	
9	60	674	
10	55	684	
11	50	698	
12	45	715	
13	40	735	$Na_2 \parallel SO_4, WO_4$
14	35	755	
15	30	775	
16	25	792	

TABLE 2

Fusibility of the System Na_2SO_4–Na_2WO_4

Expt. No.	Na_2WO_4 (%)	Temp. of appearance of first crystals	Solid phase
1	0	695	
2	5	670	
3	10	648	
4	15	625	Na_2WO_4
5	18	615	
6	20	607	
7	20.5	605	Na_2WO_4, $PbWO_4$
8	21.5	614	
9	23	627	
10	25	645	
11	30	689	
12	35	724	
13	40	760	$PbWO_4$
14	45	790	
15	50	825	
16	55	860	
17	60	887	
18	65	918	

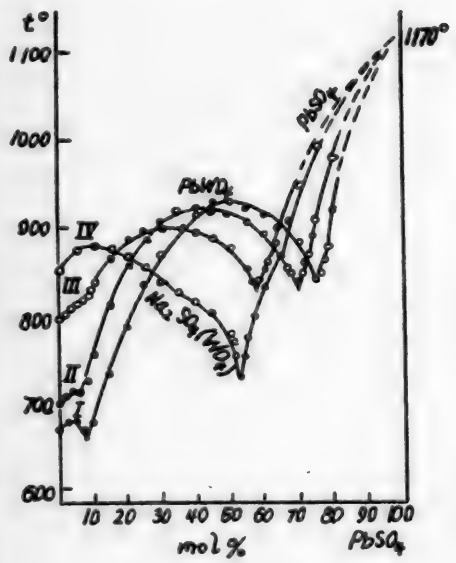

Fig. 3.

I) [75% Na_2WO_4 – 25% Na_2SO_4] ⟶ $PbSO_4$,
II) [50% Na_2WO_4 – 50% Na_2SO_4] ⟶ $PbSO_4$,
III) [25% Na_2WO_4 – 75% Na_2SO_4] ⟶ $PbSO_4$ and
IV) [90% Na_2SO_4 – 10% Na_2WO_4] ⟶ $PbSO_4$.

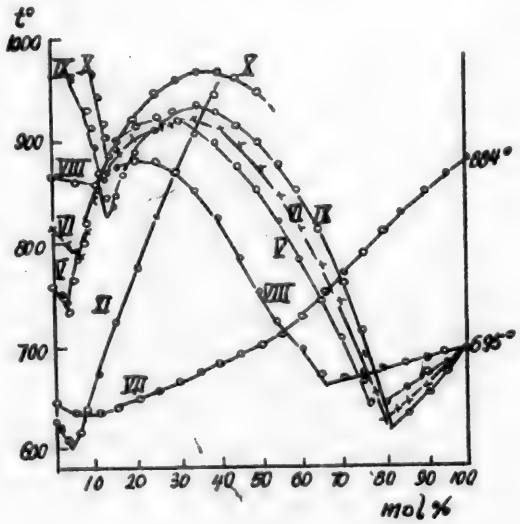

Fig. 4.

V) [50% Na_2SO_4 – 50% $PbSO_4$] ⟶ Na_2WO_4,
VI) [40% Na_2SO_4 – 60% $PbSO_4$] ⟶ Na_2WO_4,
VII) [90% Na_2WO_4 – 10% $PbWO_4$] ⟶ Na_2SO_4,
VIII) [75% Na_2SO_4 – 25% $PbSO_4$] ⟶ Na_2WO_4,
IX) [25% Na_2SO_4 – 75% $PbSO_4$] ⟶ Na_2WO_4,
X) [85% $PbSO_4$ – 15% $PbWO_4$] ⟶ Na_2WO_4,
XI) [15% $PbWO_4$ – 85% Na_2WO_4] ⟶ $PbSO_4$.

TABLE 3

Diagonal Section of Na_2WO_4–$PbSO_4$

Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase
1	0	695	Na_2WO_4
2	5	668	
3	10	638	$Na_2 \parallel SO_4, WO_4$
4	12	628	
5	14	617	$Na_2 \parallel SO_4, WO_4, PbWO_4$
6	15	630	
7	18	658	
8	20	688	
9	25	748	
10	30	804	
11	35	860	
12	40	897	
13	45	925	$PbWO_4$
14	50	948	
15	55	952	
16	60	949	
17	65	936	
18	70	921	
19	75	895	
20	76	886	
21	77	876	$PbWO_4$, α–$PbSO_4$
22	78	868	α–$PbSO_4$
23	79	870	
24	80	890	β–$PbSO_4$
25	85	980	

TABLE 4

Diagonal Section of Na_2SO_4–$PbWO_4$

Expt. No.	$PbWO_4$ (%)	Temp. of appearance of first crystals	Solid phase
1	0	884	
2	5	883	Na_2SO_4
3	10	870	
4	12	872	
5	15	860	Na_2SO_4, $PbWO_4$
6	20	882	
7	25	898	
8	30	909	
9	35	916	
10	40	922	$PbWO_4$
11	45	932	
12	50	950	
13	55	962	
14	60	975	
15	65	990	

the system Na_2WO_4–$PbWO_4$ is the first to have been published. This system exhibits a simple eutectic at 605° and 25% $PbWO_4$ (Table 2, Figure 1, IV).

The crystallization surfaces of all the reciprocal systems were determined by an investigation of 2 diagonal and 11 internal sections. The distribution of the internal sections is represented in Figure 2.

TABLE 5

Section I – [75% Na_2WO_4 – 25% Na_2SO_4] ⟶ $PbSO_4$

Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase	Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase
1	0	667		13	45	926	
2	1	672		14	50	928	
3	3	677		15	55	925	$PbWO_4$
4	5	678	$Na_2 \parallel SO_4, WO_4$	16	60	916	
5	7	670		17	65	906	
6	10	675		18	70	884	
7	15	730		19	75	836	$PbWO_4$, x – $PbSO_4$
8	20	785		20	76	850	α – $PbSO_4$
9	25	832		21	77	864	
10	30	869	$PbWO_4$	22	78	880	β – $PbSO_4$
11	35	898		23	80	924	
12	40	916					

TABLE 6

Section II – [50% Na_2WO_4 – 50% Na_2SO_4] ⟶ $PbSO_4$

Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase
1	0	690	
2	2	704	
3	4	710	$Na_2 \| SO_4, WO_4$
4	5	712	
5	6	712	
6	7	708	$Na_2 \| SO_4, WO_4$ –
7	8	724	– $PbWO_4$
8	10	752	
9	15	810	
10	20	858	
11	25	888	
12	30	905	
13	35	918	
14	40	922	$PbWO_4$
15	45	922	
16	50	918	
17	55	908	
18	60	893	
19	65	867	
20	67	855	
21	68	846	
22	70	836	
23	71	848	
24	72	860	α–$PbSO_4$
25	73	868	
26	74	890	
27	75	910	β–$PbSO_4$
28	80	980	

TABLE 7

Section III – [25% Na_2WO_4 – 75% Na_2SO_4] ⟶ $PbSO_4$

Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase
1	0	794	
2	1	800	
3	3	807	
4	5	814	$Na_2 \| SO_4, WO_4$
5	7	818	
6	8	819	
7	9	826	
8	10	835	
9	15	865	
10	20	884	
11	25	896	
12	30	902	$PbWO_4$
13	35	900	
14	40	895	
15	45	888	
16	50	875	
17	55	852	
18	57	839	
19	59	840	
20	60	852	α – $PbSO_4$
21	61	860	
22	62	868	
23	63	882	
24	64	900	β – $PbSO_4$
25	65	915	
26	70	955	

TABLE 8

Section IV – [90% Na_2SO_4 – 10% Na_2WO_4] ⟶ $PbSO_4$

Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase	Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase
1	0	850		12	51	766	
2	5	876		13	52	748	$Na_2 \| SO_4, WO_4$
3	10	880		14	53	725	$Na_2 \| SO_4, WO_4$–$PbSO_4$
4	15	876		15	54	748	
5	20	868		16	55	773	
6	25	855	$Na_2 \| SO_4, WO_4$	17	57	800	α – $PbSO_4$
7	30	838		18	60	834	
8	35	825		19	65	868	α, β – $PbSO_4$
9	40	815		20	67	908	
10	45	800		21	70	950	β – $PbSO_4$
11	50	776		22	75	995	

TABLE 9

Section V – [50% Na_2SO_4 – 50% $PbSO_4$] ⟶ Na_2WO_4

Expt. No.	Na_2WO_4 (%)	Temp. of appearance of first crystals	Solid phase
1	0	775	β – $PbSO_4$
2	1	750	
3	2	740	β–$PbSO_4$–$Na_2\|\|SO_4, WO_4$
4	3	730	$Na_2\|\|SO_4$, WO_4
5	4	763	
6	5	785	
7	7	798	$Na_2\|\|SO_4$, WO_4–$PbWO_4$
8	8	818	
9	10	850	
10	15	895	
11	20	913	
12	25	920	
13	30	918	
14	35	910	
15	40	896	
16	45	875	$PbWO_4$
17	50	850	
18	55	820	
19	60	785	
20	65	750	
21	70	707	
22	75	663	
23	77	642	
24	80	645	
25	85	658	$Na_2\|\|SO_4$, WO_4
26	90	672	
27	95	685	
28	100	695	Na_2WO_4

TABLE 10

Section VI – [60% $PbSO_4$ – 40% Na_2SO_4] ⟶ Na_2WO_4

Expt. No.	Na_2WO_4 (%)	Temp. of appearance of first crystals	Solid phase
1	0	816	
2	4	803	$PbSO_4$
3	5	799	
4	7	792	
5	8	816	
6	10	848	
7	15	884	
8	20	905	
9	25	916	
10	30	924	
11	35	925	
12	40	915	
13	45	900	$PbWO_4$
14	50	875	
15	55	846	
16	60	815	
17	65	780	
18	70	745	
19	75	690	
20	78	650	
21	80	630	$PbWO_4$–$Na_2\|\|SO_4, WO_4$
22	83	638	
23	85	644	
24	90	660	$Na_2\|\|SO_4$, WO_4
25	95	676	
26	100	695	

TABLE 11

Section VII – [90% Na_2WO_4 – 10% $PbWO_4$] ⟶ Na_2SO_4

Expt. No.	Na_2SO_4	Temp. of appearance of first crystals	Solid phase
1	0	647	
2	5	638	
3	10	636	
4	15	643	
5	20	650	$Na_2\|\|SO_4$, WO_4
6	25	657	
7	30	666	
8	35	675	
9	40	684	
10	45	692	
11	50	715	
12	55	730	
13	60	748	
14	65	770	
15	70	789	$Na_2\|\|SO_4$, WO_4
16	75	812	
17	80	830	
18	85	850	
19	90	868	
20	100	884	Na_2SO_4

TABLE 12

Section VIII – [75% Na_2SO_4 – 25% $PbSO_4$] ⟶ Na_2WO_4

Expt. No.	Na_2WO_4 (%)	Temp. of appearance of first crystals	Solid phase
1	0	865	Na_2SO_4
2	5	862	$Na_2 \| SO_4, WO_4$
3	10	859	
4	13	870	
5	15	875	
6	20	880	
7	25	878	
8	30	870	
9	35	850	
10	40	824	
11	45	785	$PbWO_4$
12	50	753	
13	55	724	
14	60	695	
15	65	670	
16	70	666	
17	75	670	
18	80	674	
19	85	680	$Na_2 \| SO_4, WO_4$
20	90	685	
21	95	690	
22	100	695	Na_2WO_4

TABLE 13

Section IX – [25% Na_2SO_4 – 75% $PbSO_4$] ⟶ Na_2WO_4

Expt.	Na_2WO_4	Temp. of appearance of first crystals	Solid phase
1	0	–	
2	5	960	
3	8	930	β – $PbSO_4$
4	9	914	
5	10	895	
6	11	868	β–$PbSO_4$, α–$PbSO_4$
7	12	860	
8	13	844	α–$PbSO_4$
9	14	834	
10	15	846	
11	17	868	
12	20	890	
13	25	912	
14	30	929	
15	35	932	
16	40	930	
17	45	915	
18	50	898	
19	55	876	$PbWO_4$
20	60	848	
21	65	810	
22	70	760	
23	75	710	
24	80	645	
25	85	634	
26	90	650	$Na_2 \| SO_4, WO_4$
27	95	672	
28	100	695	Na_2WO_4

TABLE 14

Section X – [85 % $PbSO_4$ – 15% $PbWO_4$] ⟶ Na_2WO_4

Expt. No.	Na_2WO_4	Temp. of appearance of first crystals	Solid phase
1	10	964	
2	11	944	
3	12	916	$PbSO_4$
4	13	904	
5	15	892	
6	20	920	
7	25	944	
8	30	958	$PbWO_4$
9	35	965	
10	40	964	
11	45	960	
12	50	945	

TABLE 15

Section XI – [15% $PbWO_4$ – 85% Na_2WO_4] ⟶ $PbSO_4$

Expt. No.	$PbSO_4$ (%)	Temp. of appearance of first crystals	Solid phase
1	0	625	Na_2WO_4
2	1	620	$Na_2 \| SO_4, WO_4$
3	3	612	
4	5	615	
5	7	638	
6	10	675	
7	15	725	
8	20	775	$PbWO_4$
9	25	824	
10	30	868	
11	35	907	
12	40	944	

TABLE 16

No. of fields	Field of crystallization	Area (in % of total area of square)	
	Solid solution		
I	$Na_2 \| SO_4, WO_4$	13.5	
II	$PbWO_4$	75.6	
III	β–$PbSO_4$	1.8	10.9
IV	α–$PbSO_4$	9.1	

The diagonal section of Na_2WO_4–$PbSO_4$ (Table 3, Fig.1, III) intersects three cyrstallization fields; the liquidus line correspondingly consists of three branches: the $NaWO_4$ branch, intersecting the $PbWO_4$ crystallization branch at 617° and 14 % $PbSO_4$; and the $PbSO_4$ crystallization branch, intersecting the $PbWO_4$ branch at 860° and 78.5% $PbSO_4$.

The diagonal section of Na_2SO_4–$PbWO_4$ (Table 4, Figure 1,I) has the character of a binary system with a simple eutectic at 860° and 15% $PbWO_4$. The liquidus line has a small sloping portion between 30 and 40% $PbWO_4$.

Section I – [75% $NaWO_4$–25% Na_2SO_4] ⟶ $PbSO_4$ (Table 5, Figure 3) passes through 3 crystallization fields: The solid solutions $Na_2 \| SO_4, WO_4$; lead tungstate and lead sulfate. Eutectic points are: $Na_2 \| SO_4, WO_4$–$PbWO_4$ at 660° and 9% $PbSO_4$; $PbSO_4$–$PbWO_4$ at 836° and 75% $PbSO_4$. A polymorphic transformation occurs at 868° on the $PbSO_4$ crystallization branch.

Section II – [50% Na_2WO_4–50% Na_2SO_4] ⟶ $PbSO_4$ (Table 6, Fig 3) – resembles the first section. Eutectic points are: $Na_2 \| SO_4, WO_4$–$PbWO_4$, at 708° and 7% $PbSO_4$; $PbWO_4$–$PbSO_4$, at 830° and 69.9% $PbSO_4$. Polymorphic transformation of $PbSO_4$ at 868°.

Section III – [25% Na_2WO_4–75% Na_2SO_4] ⟶ $PbSO_4$ (Table 7, Fig.3). – is similar to sections I and II. Eutectic points are: $Na_2 \| SO_4, WO_4$–$PbWO_4$

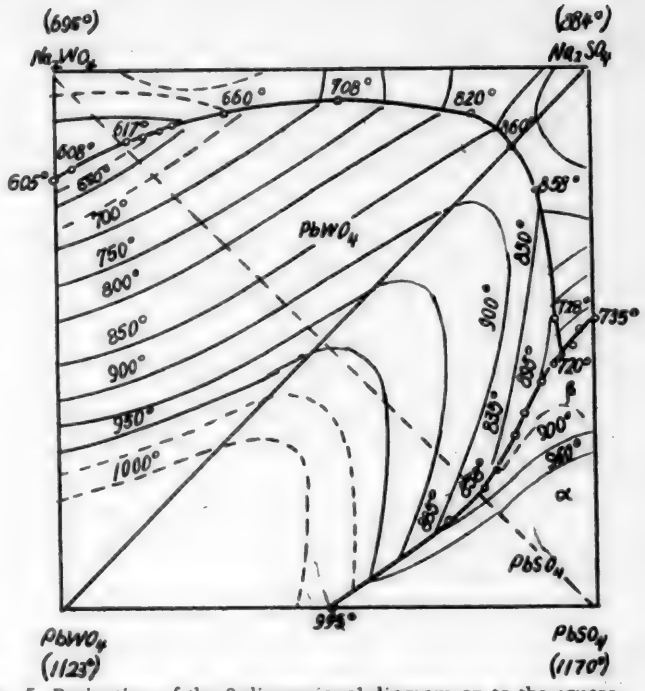

Fig. 5. Projection of the 3-dimensional diagram on to the square of compositions of the reciprocal system.

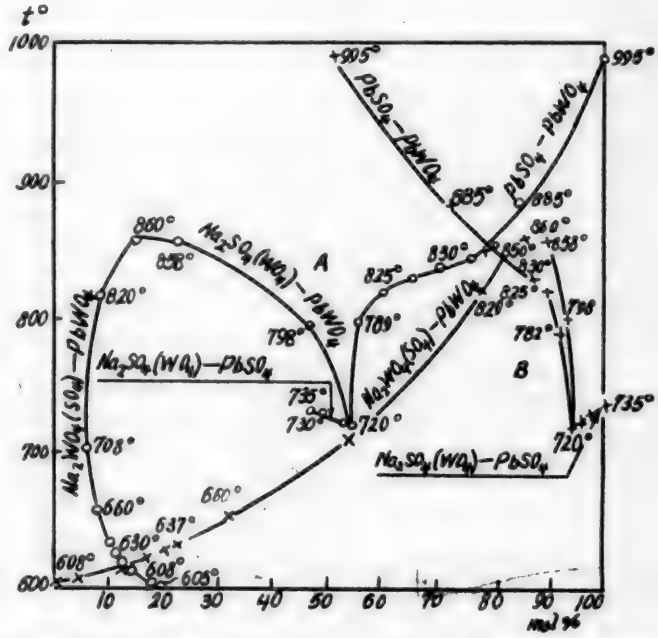

Fig. 6. Projections of the eutectic lines. A) on to the Na_2WO_4–$PbWO_4$ side; B) on to the $PbWO_4$–$PbSO_4$ side.

at 820° and 8.5% $PbSO_4$; $PbWO_4$–$PbSO_4$ at 825° and 58% $PbSO_4$. Transition from the α- to the β-modification of $PbSO_4$ at 868°.

Section IV – [90% Na_2SO_4 – 10% Na_2WO_4] ⟶ $PbSO_4$ (Table 8, Fig.3) – only passes through 2 fields of crystallization of $Na_2 \| SO_4$, WO_4 and $PbSO_4$. The eutectic lies at 725° and 53% $PbSO_4$. Transition of α-$PbSO_4$ into β-$PbSO_4$ at 868°.

Section V – [50% Na_2SO_4 – 50% $PbSO_4$] ⟶ Na_2WO_4 (Table 9, Figure 4) – intersects 4 crystallization fields: β-$PbSO_4$, $Na_2 \| SO_4$, WO_4, $PbWO_4$, $Na_2 \| SO_4$, WO_4. The respective eutectic points are: β-$PbSO_4$–$Na_2 \| SO_4$, WO_4 at 730° and 3% Na_2WO_4; $Na_2 \| SO_4$, WO_4–$PbWO_4$ at 798° and 7% Na_2WO_4; and $PbWO_4$–$Na_2 \| SO_4$, WO_4 at 637° and 77.5% Na_2WO_4.

Section VI – [60% $PbSO_4$ – 40% Na_2SO_4] ⟶ Na_2WO_4 (Table 10, Fig.4) – intersects the following crystallization fields: $PbSO_4$, $PbWO_4$ and $Na_2 \| SO_4$, WO_4. The eutectic points are: $PbSO_4$–$PbWO_4$ at 789° and 7.5% Na_2WO_4; $PbWO_4$–$Na_2 \| SO_4$, WO_4 at 630° and 79.5% Na_2WO_4.

Section VII – [90% Na_2WO_4 – 10% $PbWO_4$] ⟶ Na_2SO_4 (Table 11, Fig.4) – is a control section; as seen on Figure 4, it is entirely similar to the system Na_2SO_4–Na_2WO_4 with a minimum at 636°.

Section VIII – [75% Na_2SO_4 – 25% $PbSO_4$] ⟶ Na_2WO_4 (Table 12, Fig. 4) – intersects the fields of the crystallization surfaces: twice $Na_2 \| SO_4$, WO_4 and $PbWO_4$. Eutectics: At 10% Na_2WO_4 and 858°, and at 67% Na_2WO_4 and 664°.

Section IX – [25% Na_2SO_4 – 75% $PbSO_4$] ⟶ Na_2WO_4 (Table 13, Fig. 4) – resembles section VI. Eutectic points: $PbSO_4$–$PbWO_4$ at 825° and 13.5% Na_2WO_4; $PbWO_4$–$Na_2 \| SO_4$, WO_4 at 622° and 81.5% $NaWO_4$. Transition of α-$PbSO_4$ into β-$PbSO_4$ at 868°.

Section X – [85% $PbSO_4$ – 15% $PbWO_4$] ⟶ Na_2WO_4 (Table 14, Fig.4) – was investigated to 50% Na_2WO_4; on this portion it intersects two crystallization surfaces: $PbSO_4$ and $PbWO_4$. The eutectic lies at 885° and 14% Na_2WO_4.

Section XI – [15% $PbWO_4$ – 85% Na_2WO_4] ⟶ $PbSO_4$ (Table 15, Fig.4) – was investigated to 40% $PbSO_4$; in this range it intersects two crystallization suffaces. The eutectic is at 608° and 4% $PbSO_4$.

On the basis of the data for the fusibility of the binary systems (sides of the square) diagonal sections and internal sections, a projection diagram was plotted on to the square of compositions of the reciprocal system (Figure 5). It is assumed that the liquidus surface consists of four crystallization fields: The solid solutions $Na_2 \| SO_4$, WO_4, $PbWO_4$, α- and β-$PbSO_4$. The corresponding areas of the crystallization fields are presented in Table 16.

The projections of the eutectics on the sides Na_2WO_4–$PbWO_4$ and $PbWO_4$–$PbSO_4$ (Figure 6) meet in a ternary eutectic point at 720° and the composition: 48.5% $PbSO_4$, 5.5% $PbWO_4$ and 46% Na_2SO_4. The diagonal section Na_2SO_4–$PbWO_4$ has the character of a binary system with a simple eutectic. The eutectic point lies at 860° and 15% $PbWO_4$ (Figure 5) and is the saddle point of the reciprocal system.

Due to the lack of data for the heats of formation of lead and sodium tungstates, it is impossible to calculate the thermal effect of the double decomposition; it is clear, however, from the character of the diagram that the equilibrium is sharply shifted in the direction of formation of lead tungstate and sodium sulfate, i.e. in the direction of combination of ions with similar radii (Beketov [3], Gustavson [4]).

According to the classification of A. G. Bergman and N. S. Dombrovskaya [5], the system is an irreversible-reciprocal one with the stable diagonal Na_2SO_4–$PbWO_4$, although the displacement of the crest in the crystallization field of $PbWO_4$ in the direction of $PbSO_4$ points to a certain degree of reversibility of the reaction.

SUMMARY

1. A study was made by the visual-polythermal method of the liquidus surface of the reciprocal system, Na, Pb $\|$ SO_4, WO_4.

2. The system is a simple irreversible-reciprocal one with the stable diagonal Na_2SO_4–$PbWO_4$.

3. The liquidus surface of the system comprises four fields of crystallization: The solid solutions $Na_2 \| SO_4$, WO_4, $PbWO_4$, α- and β-$PbSO_4$.

4. The system is characterized by one ternary eutectic at 720° and the composition: 48.5% $PbSO_4$, 5.5% $PbWO_4$, 46% Na_2SO_4; and by one saddle point at 860°, 15% $PbWO_4$ and 85% Na_2SO_4.

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Received December 29, 1950

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EFFECT OF TEMPERATURE ON THE REDUCTION OF ORGANIC COMPOUNDS AT THE DROPPING MERCURY ELECTRODE

Z. B. Kuznetsova and I. A. Korshunov

In the practice of polarographic analysis it is known that the magnitude of the diffusion current largely depends on the operating temperature. The effect of the temperature on the diffusion current may be represented by Ilkovic's equation:

$$i_d = 605\, n D^{1/2} m^{2/3} t^{1/6} C, \qquad (1)$$

where i_d is the diffusion current in μA); n is the number of electrons participating in the reduction of one molecule; D is the diffusion coefficient of the molecules undergoing reduction (in $cm^2 \cdot sec^{-1}$); m is the weight of mercury flowing from the capillary per second (in mg); t is the period of formation (in seconds) of each drop of mercury; C is the concentration of reacting substance (in mmole/liter).

Starting from the above expression Kolthof and Lingane [1] obtained the following expression for the temperature coefficient of the diffusion current of the ions undergoing reduction (for temperatures around 25°C):

$$\frac{1}{i_d} \cdot \frac{di_d}{dT} = 0.0026 + \frac{1}{2\lambda_0} \cdot \frac{d\lambda_0}{dT}, \qquad (2)$$

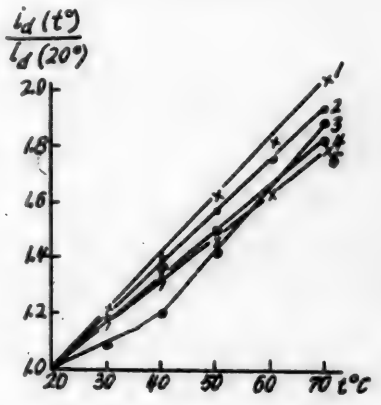
where λ_0 is the equivalent ionic conductivity at infinite dilution and for the absolute temperature T.

The first term on the right-hand side of the equation is much smaller than the second; consequently the temperature coefficient is mainly a function of the temperature coefficient of the equivalent conductivity of the ions being reduced. The temperature coefficients of the equivalent conductivity of the majority of ions lie within the range 0.02-0.027°$^{-1}$ with the exception of H^+ and OH^-, whose respective values are 0.0157 and 0.018°$^{-1}$. Hence the temperature coefficient of the diffusion current of the majority of ions must have a value within the range of 1.3-1.6% per degree and must be close to 1.05% per degree for dissociation of hydrogen ions.

The experimental values of the temperature coefficients of the diffusion current of ions of various metals for temperatures of 20 to 50° vary within the range of 1.3 to 2.3% per degree [1] and are in sufficiently good agreement with the theoretical values.

Diffusion currents of organic compounds as functions of the temperature have not been investigated.

In this paper we describe the results of a study of the effect of temperature on the polarographic reduction of benzaldehyde, butyraldehyde, chloracetamide, phenyl trichloroacetate, dibutylphthalate, maleic acid, and fumaric acid.



Influence of temperature on the reduction of organic compounds.
1) Benzaldehyde; 2) butyraldehyde; 3) phenyl trichloroacetate; 4) chloracetamide; 5) maleic and fumaric acids.

The investigations were performed on the M-7 visual polarograph of the Gorky Chemical Research Institute [2,3]. Prior to the plotting of the polarograms the electrolyzer containing the solution of the test substance was placed in a thermostat in which a constant temperature was maintained with the help of a toluene thermoregulator and a variable current relay. The rate of flow of the mercury from the capillary was uniform throughout the investigation at one drop per four seconds. The characteristic of the capillary utilized in the work was $m^{2/3}t^{1/6} = 0.78$

$mg^{2/3}\ sec^{-1/2}$. All the values of diffusion current on the diagram and in the tables have been converted for a capillary with a characteristic of 1.0 $mg^{2/3}\ sec^{-1/2}$. The current strength was measured with the help of a mirror galvanometer whose current sensitivity was $0.58 \cdot 10^{-9}$ A/mm/m. The anode was a saturated calomel cell whose potential was taken as zero. The applied voltage was measured with the help of a voltmeter accurate to 0.01 V.

The temperature dependence of the diffusion current of the investigated organic compounds is given in the diagram. The effect of temperature on the diffusion current and half-wave potential of butyraldehyde and maleic acid is shown by the experimental data presented in Tables 1 and 2.

TABLE 1

Effect of Temperature on the Reduction of Butyraldehyde in $(CH_3)_4NI$. C = 4.8 mmoles/liter

t° C	i_d μA	$\frac{i_d(t°)}{i_d(20°)}$	$-E_{1/2}$ B
20	15.3	1.00	1.88
30	18.0	1.18	1.88
40	25.5	1.67	1.88
50	29.6	1.93	1.90
60	30.0	1.96	1.88
70	30.6	2.00	1.86

TABLE 2

Effect of Temperature on the Reduction of Maleic Acid in $(CH_3)_4NI$. C = 4.0 mmoles/liter

t° C	i_d μA	$\frac{i_d(t°)}{i_d(20°)}$	$-E_{1/2}$ B
20	11.6	1.00	0.95
30	13.9	1.20	0.92
40	15.3	1.32	0.93
50	17.0	1.47	0.92
60	20.4	1.76	0.93
70	24.5	2.12	0.93

The diagram and the tables show that the temperature coefficient of all the investigated compounds with the exception of phenyl trichloroacetate remains constant with change of temperature from 20 to 70°, and that there is a straight-line dependence of the ratio of the diffusion current at a given temperature to the value at 20° on the temperature. The slope of the straight line varies for each compound investigated and varies slightly with the structure of the compound. In the case of benzaldehyde, for instance, the relation between $\frac{i_d(t°)}{i_d(20°)}$ and the temperature is represented by the formula:

$$\frac{i_d(t°)}{i_d(20°)} = 0.0021t \qquad (3)$$

while for fumaric and maleic acids it is represented by:

$$\frac{i_d(t°)}{i_d(20°)} = 0.0156t. \qquad (4)$$

The temperature coefficient of the diffusion current during reduction of organic compounds in the temperature range of 20 to 70° is 1.15-1.50% per degree. The experimental values show that the temperature coefficients of the diffusion current of organic compounds only differ slightly from the temperature coefficients of the diffusion current of the various ions and are close to the theoretical magnitude.

In the practice of polarography the temperature should be kept constant to within at least ±0.5° in order to ensure that the deviations of the diffusion current due to the temperature change should not exceed ±1.0%.

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Received January 18, 1951

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PHYSICOCHEMICAL ANALYSIS OF THE SYSTEMS PHENOL-MONOCHLORACETIC ACID AND PHENOL-TRICHLORACETIC ACID

V. V. Udovenko, R. P. Airapetova and V. T. Malakhova

It has previously been shown [1] that the components do not react with each other in the system phenol-formic acid. It was of interest to investigate the effect of replacing formic acid by stronger acids. We, therefore, carried out an investigation, by the method of thermal analysis and of viscosity measurements, of the systems: phenol-monochloracetic acid and phenol-trichloracetic acid.

The acids were purified by recrystallization from benzene followed by distillation. The boiling point of the monochloracetic acid was 186.3° (765 mm), and that of the trichloracetic acid was 192.8° (731 mm). The phenol was purified by repeated distillation. It boiled at 180.4° (730 mm). The pure substances were stored in sealed tubes.

Thermal analysis was carried out visually as described in the previous paper [1]. The viscosity and density were measured at 50, 60 and 75°. The phase diagram of the system phenol-monochloracetic acid is represented in Figure 1. It contains only one eutectic whose composition corresponds to 57 mole-% phenol; the melting point is 3°. We succeeded in following the crystallization of the eutectic in mixtures containing from 49 to 68.7% phenol. Kendall also reports that the phase diagram of this system contains one eutectic [3].

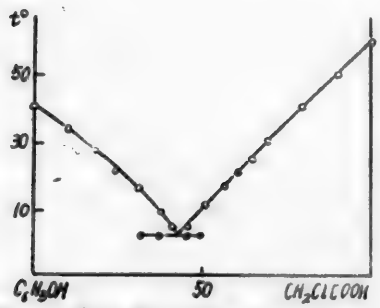

Fig. 1. Phase diagram of the system phenol-monochloracetic acid.

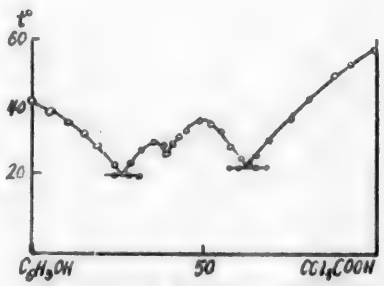

Fig. 2. Phase diagram of the system phenol-trichloracetic acid.

Results of viscosity and density measurements of the system phenol-monochloracetic acid are preented in Table 1, from which viscosity isotherms were plotted. In the high-concentration region these isotherms pass through a diffuse maximum, and at low concentrations through a very ill-defined minimum. The form of the viscosity isotherms of the system phenol-monochloracetic acid is similar to that in the system nitrobenzene-formic acid [2]. The presence of a weak maximum on the viscosity isotherms of the system phenol-monochloracetic acid testifies to reaction between the components in the liquid phase. The weakness of the reaction prevents the formation of a compound crystallizing in the solid state.

The diagram of thermal analysis of the system phenol-trichloracetic acid is shown in Figure 2. In this system the components interact chemically with formation of two crystalline compounds. The distectic maxima on the diagram correspond precisely to an equimolecular compound and to a compound containing two molecules of phenol per molecule of acid. The phase diagram also contains three eutectics. The eutectic with 73.9 mole-% phenol melts at 20°. We observed the melting point of this eutectic in the concentration range of 68.4 to 76.6 mole-% phenol. The eutectic containing 60.6 mole-% phenol melts at 26°, and that containing 37.9 mole-% phenol melts at 22°. We were able to follow the eutectic melting point of the latter in mixtures containing from 30.8 to 43.2% mole-% phenol. We repeated the thermal analysis of the system phenol-trichloracetic acid several times and each

TABLE 1

System Phenol-Monochloracetic Acid

Mole-% Phenol	Viscosity (centipoises)			Density		
	50°	60°	75°	50°	60°	75°
100	3.336	2.521	1.742	1.0499	1.0399	1.0280
90.30	3.353	2.527	1.763	1.0745	1.0638	1.0525
82.16	3.338	2.524	1.768	1.0943	1.0856	1.0736
75.67	3.308	2.508	1.771	1.1133	1.1053	1.0918
70.37	3.277	2.505	1.768	1.1300	1.1204	1.1116
67.35	3.242	2.497	1.765	1.1380	1.1307	1.1148
60.60	3.203	2.493	1.761	1.1562	1.1491	1.1324
51.13	3.142	2.441	1.762	1.1916	1.1852	1.1661
40.50	3.121	2.435	1.782	1.2212	1.2119	1.1954
30.59	3.112	2.431	1.790	1.2596	1.2500	1.2320
26.00	3.103	2.427	1.803	1.2826	1.2718	1.2548
19.18	3.113	2.428	1.809	1.3120	1.2982	1.2808
11.28	3.125	2.436	1.819	1.3327	1.3230	1.3052
0	–	2.442	1.835	–	1.3720	1.3520

time we obtained the phase diagram shown in Figure 2. Furthermore, compounds with the compositions $C_6H_5OH \cdot CCl_3COOH$ and $2C_6H_5OH \cdot CCl_3COOH$ were isolated and recrystallized from benzene. The pure compounds form white crystals melting at 37.8° and 31.2° respectively.

Thermal analysis of the system phenol-trichloracetic acid has been carried out by Kendall [3] and by Puschin and Rikovcki [4]. Their phase diagram contains only one distectic corresponding to the equimolecular compound. Kendall gives 37.6° as the melting point of the equimolecular compound. The failure of Kendall and of Puschin and Rikovcki to observe a second distectic can be explained by the fact that they only studied a comparatively small number of points.

Results of measurements of the viscosity and density of the system phenol-trichloracetic acid are presented in Table 2. The viscosity isotherms of this system have an irrational maximum which is shifted in the acid direction with rising temperature. Consequently the interaction of the components in this system is reflected both on the phase diagram and on the viscosity isotherms. In the system phenol-monochloracetic acid, however, the weaker interaction of the components is only reflected on the viscosity isotherms.

TABLE 2

System Phenol-Trichloracetic Acid

Mole-% Phenol	Viscosity (centipoises)			Density		
	50°	60°	75°	50°	60°	75°
100	3.278	2.494	1.737	1.0518	1.0427	1.0290
91.17	3.569	2.721	1.865	1.0954	1.0902	1.0754
85.44	3.811	2.900	1.977	1.1382	1.1324	1.1184
76.00	4.127	3.127	2.141	1.1990	1.1901	1.1721
69.28	4.342	3.248	2.238	1 2754	1.2030	1.2004
59.25	4.683	3.482	2.386	1.2942	1.2869	1.2704
50.25	4.779	3.666	2.513	1.3445	1.3323	1.3150
40.32	5.012	3.778	2.617	1.4015	1.3917	1.3638
33.05	5.085	3.886	2.706	1.4445	1.4337	1.4160
24.50	5.126	3.894	2.754	1.4863	1.4770	1.4586
18.34	5.115	3.878	2.792	1.5195	1.5074	1.4863
10.05	5.083	3.837	2.815	1.5667	1.5462	1.5330
0.	4.797	3.786	2.779	1.6181	1.6048	1.5776

SUMMARY

1. The systems phenol-monochloracetic acid and phenol-trichloracetic acid have been examined by the method of thermal analysis and by measurements of viscosity and density at 50°, 60° and 75°.

2. The system phenol-trichloracetic acid is found to form solid crystalline compounds with the compositions $C_6H_5OH \cdot CCl_3COOH$ and $2C_6H_5OH \cdot CCl_3COOH$.

3. The interaction of the components in the two systems is shown to be reflected in the form of the viscosity isotherms.

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Received March 16, 1951

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THE ELECTRIC CONDUCTIVITY OF HYDROCARBON SOLUTIONS OF IODINE

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As far as we are aware the electric conductivity of hydrocarbon solutions of iodine has only received attention in the studies of Brunner and Rabinovich.

Due to the roughness of the method of measurement, Brunner [1] was unable to detect any appreciable conductivity of the iodine solutions in toluene, whereas Rabinovich [2] found that benzene solutions, up to high concentrations (16.8%), conduct current nearly twice as badly as the original benzene whose specific electric conductivity was $7.8 \cdot 10^{-13}$ reciprocal ohms /cm.

These data, especially Rabinovich's, have not been verified. It appeared uncertain that iodine could lower the electric conductivity of benzene in which, incidentally, it could not dissolve at room temperature in such high (16.8%) concentration.

In the investigation of the mechanism of corrosion of metals in hydrocarbon solutions of iodine [3-5] we had to know the specific electric conductivity of such solutions and its dependence on the potential of the electric field. This also prompted us to carry out the determinations.

EXPERIMENTAL

We investigated the specific electric conductivity of isooctane and benzene solutions of iodine.

The isooctane [d_4^{20}–0.700; b. p. (765 mm) 97-99°] and benzene [d_4^{20}–0.874; b.p. (765 mm) 80.5°] were thoroughly dried over sodium.

The iodine (chemically pure) was twice sublimed over KI and BaO, after which it was again sublimed and dried over P_2O_5.

The high-voltage apparatus used by us in the measurements is sketched in Fig. 1. This apparatus permitted the application to the electrodes of potentials of 300 to 4000 V and the attainment of an electric field potential of 40,000 V/cm. The source of current up to 300 V was a BAS-80 battery.

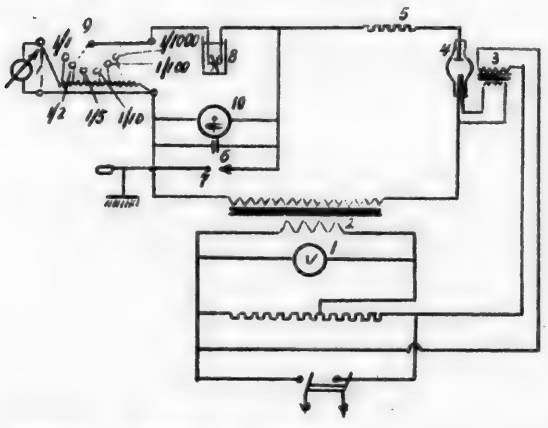


Figure 1. High-voltage apparatus
1 - Guard voltmeter; 2 - step-up transformer; 3 - heat transformer; 4 - VCh-2000 thermionic rectifier; 5 - 30,000 ohms resistance; 6 - two microfarads condenser; 7 - discharger; 8 - cell for determination of electric conductivity; 9 - Ayrton shunt and 10^{-9} A galvanometer; 10 - static voltmeter.

Currents were measured with a mirror galvanometer with a scale division equivalent to $1.53 \cdot 10^{-9}$ A.

The glass conductivity cell was provided with Rogovsky platinum electrodes, fixed parallel to each other and 1 mm apart; their inner working surface was polished.

The vessel containing the test liquid was placed in a "thermostat-desiccator" which consisted of a Plexiglass housing, , heated by an electric lamp turned upside down, containing sulfuric acid, phosphorus pentoxide and other desiccants. This simple device ensured constancy of temperature and, what is particularly important, provided protection against current leakages due to condensation of water on the walls of the vessel.

After distilling the hydrocarbon into the cell and determining its specific conductivity, the weighed amount of iodine was dissolved in it (when the conductivity had been found minimal). The volt-ampere characteristic of the .

solution was then plotted. The conductivity of a 0.0078 N solution was measured; the low dilution was due to the poor solubility of iodine in isooctane. The volt-ampere characteristic was plotted for at least three freshly prepared solutions, and the results were only considered reliable when they substantially agreed with one another. Measurements were performed at 20°.

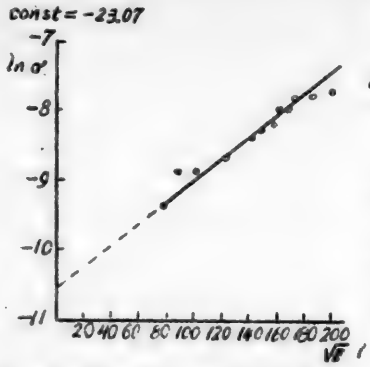


Fig. 2. Electric conductivity of isooctane solutions of iodine

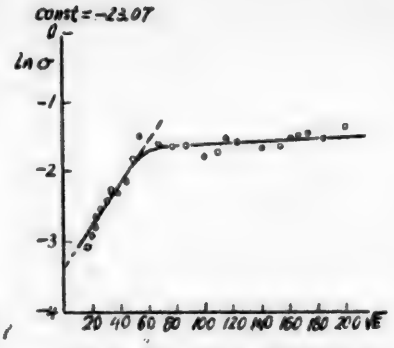


Fig. 3. Electric conductivity of benzene solutions of iodine

Evaluation of Results

The first feature which stands out is that not only is the conductivity of the benzene solution very much better than that of the original benzene (in opposition to Rabinovich's observation), but it is slightly better than that of the isooctane solution. The specific electric conductivity (σ) at E=7500 V/cm of 0.0078 N benzene solution of iodine is $1.27 \cdot 10^{-11}$ reciprocal ohm^{-1}/cm^{-1} (the σ of pure benzene is $1.28 \cdot 10^{-14}$), whereas the σ of 0.0078 N isooctane solution of iodine is $8.57 \cdot 10^{-15}$ (the σ of pure isooctane is slightly lower).

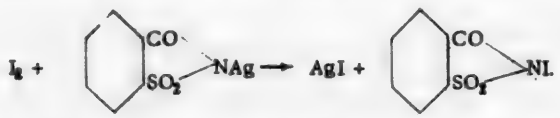
Isooctane and benzene solutions of iodine are respectively violet and brown. Hildebrand [6] draws a sharp distinction between them. He regards the violet solutions as regular solutions which "resemble ideal solutions in the sense that the thermal motion of their molecules is able to overcome the orienting tendency of the molecules, their combination or association and to bring about the completely disordered distribution existing in ideal solutions", i.e. in solutions obeying Raoult's law. But the brown or, more correctly, the gamut of red, yellow and brown solutions he regards as irregular solutions deviating from Raoult's law by virtue of the inherent tendency of their molecules to associate and solvate. In fact a series of investigators has correlated the solvation of iodine in the brown solutions with the electrolytic dissociation therein of the I_2 molecules.

Walden [7,8] was the first to suggest that the conductivity of the brown solutions of iodine was caused by dissociation according to the scheme:

(1) $I_2 \rightleftharpoons I^+ + I^-$ and (2) $2I_2 \rightleftharpoons 3I^- + I^{+++}$.

This concept of Walden's found support in the work of Feigl and Chargaff as well as of Ushakov.

Feigl and Chargaff [9] treated the brown solutions, including benzene solutions, with silver saccharin and observed that a double decomposition readily took place with formation of silver iodine and "iodosaccharin".



Ushakov [10] treated alcoholic (brown) solutions of iodine with silver nitrate and established the formation of not only silver iodide but also of the nitrates of mono- and trivalent iodine; in other words he demonstrated, so to speak, the occurrence in these solutions of the following reactions:

1) $I_2 + 2AgNO_3 \rightleftharpoons INO_3 + AgI \cdot AgNO_3$;

2) $2I_2 + 6AgNO_3 \rightleftharpoons I(NO_3)_3 + 3AgI \cdot AgNO_3$.

These results led Ushakov to conclude that the iodine was dissociated in the investigated solutions in accordance with Walden's scheme; the mono- and trivalent iodine cations are linked by the equilibrium:

$$3I^+ \rightleftharpoons I^{+++} + I_2.$$

Fialkov [11] also adheres to the view that iodine is susceptible to electrolytic dissociation in solutions, especially in those where complex-formation takes place.

All these investigators had in mind the dissociation of iodine in brown solutions and were not concerned at all with the violet ones. The reaction of Feigl and Chargaff with silver saccharin proceeded much less readily in the violet solutions, in particular in petroleum ether (the closest in character to isooctane), than in the brown solutions.

In the light of the above facts the observed better conductivity of the brown benzene solutions (compared with the violet isooctane solutions) can be regarded as the consequence of the slightly higher dissociation of iodine in the former.

However, we must point out that even though this interpretation appears to be well-founded, another explanation is possible. If we assume, namely, that in the above-described conditions iodination of the hydrocarbons takes place, then we could put forward an entirely different mechanism of the conductivity of these solutions which involves the reactions:

$$1)\ RH + I_2 \rightleftharpoons RI + HI;$$

$$2)\ HI \rightleftharpoons H^+ + I^-.$$

According to this mechanism electric conductivity is the consequence of dissociation of hydrogen iodide and not of molecular iodine. The superior conductivity of benzene solutions of iodine compared with the isooctane ones can then be explained by the greater ease of iodination of benzene in comparison with that of isooctane. Such a theory is intriguing in its simplicity, for the electrolytic dissociation of hydrogen iodine seems much more probable than that of molecular iodine. Concerning the data of Feigl and Chargaff and of Ushakov, it may be suggested that they were affected by the quality of the reagents.

Comparing the number of molecules of iodine in 1 ml of the solutions in question ($4.7 \cdot 10^{18}$) with their maximum content of ions ($2.0 \cdot 10^{11}$) (see table), we can easily realize that a negligible proportion ($0.4 \cdot 10^{-7}$) of the I_2 molecules give rise to ions. Such a number could, of course, have been formed by dissociation of either I_2 or HI. A second, most interesting feature of the data is the exponential increase in the conductivity of the solutions with increasing field potential.

Number of Ions (n') in Iodine Solutions at Various Field Potentials.

Solution	E → 0	E = 3400 V/cm	E = 40,000 V/cm
Isooctane	$4.63 \cdot 10^{7}$	–	$3.36 \cdot 10^{8}$
Benzene	$2.81 \cdot 10^{10}$	$1.60 \cdot 10^{11}$	$2.00 \cdot 10^{11}$

Note: $n' = \frac{\sigma}{e \cdot w}$; $e = 1.6 \cdot 10^{-19}$ coulomb; $w = 6.9 \cdot 10^{-4}$ cm²/sec.

V = mobility of I^- in aqueous solutions*. It follows from the Avogadro number and the concentration of iodine in the solutions that one milliliter contained $4.7 \cdot 10^{18}$ molecules of I_2.

As is known, Poole [13] gave the formula: $\sigma = \sigma_0 e^{\alpha E}$ (where α is a constant), according to which the logarithm of conductivity of solid dielectrics (mica) are directly proportional to the field potential. As further investigations showed, however, Poole's formula does not fully describe the behavior of dielectrics in strong fields.

It is described more correctly by Frenkel's equation [14]. On the assumption that the conductivity of electrolytes in strong electric fields is due to the fall of ionization energy in accordance with a mechanism similar to the Schottke mechanism, i.e., that the ionization occurs not as a result of the tunnel effect (as Zener suggestions [15], as well as other authors) but of the classical "thermal" effect, Frenkel derived the equation:

$$\sigma = \sigma_0 e^{\frac{\sqrt{e^3 E/\epsilon}}{kT}}.$$

It follows from this equation that direct dependence must exist between the logarithm of the conductivity and the square root of the field potential. Frenkel, also Poole, had electronic conductivity in mind. In actuality, however, his equation is also applicable to dielectrics with ionic conductivity, such as the solutions under investigation. Evidently their ionization energy, under the influence of the electric field, is also reduced by the amount $\sqrt{e^3 E/\epsilon}$ (where e is the electronic charge, E is the field potential and ϵ is the dielectric permeability). On applying this equation to the interpretation of the experimental data we did indeed find a linear dependence of $\ln \sigma$ on $\sqrt{E}$ in the case of the isooctane solution of iodine (Fig. 2).

* The mobility of certain ions, in hexane for instance, differs slightly, according to the literature, from their mobility in aqueous solutions [12]. We have replaced the sum of the ionic mobilities in the formula $\sigma = en(w_+ + w_-)$ by the mobility of one ion, which is not of great significance, since we are only interested in the order of magnitude of n'.

Analogous measurements were carried out in 1943 by Chia Chan Pao [16] who investigated the behavior of I in the strong fields of isooctane and liquid oxygen. He obtained the same linear relation (in plots of ln σ against $\sqrt{E}$) as we did. We obtained a value of 0.27 for the tangent of the slope of the straight line in Figure 2 for the isooctane solution of iodine (using absolute units), whereas the angular coefficients of the straight lines for isooctane obtained by Chia Chan Pao were 2.5 times as large (after converting from base 10 logarithms to natural logarithms).

It should be noted that the theoretical value of this tangent is $\frac{\sqrt{e^3/\epsilon}}{kT}$. At room temperature and when $\epsilon = 1$, it is equal to 0.28, i.e., very close to our measurement on the assumption that $\epsilon = 1$. Actually, however, the dielectric permeability of a solution of iodine in isooctane must be slightly larger (approximately 2-3).

If this fact is taken into account the agreement between theory and our experimental results becomes rather worse, and the deviation is greater in the case of Pao's results. The reason for these divergencies will be considered elsewhere.

In the case of the benzene solution the dependence of ln σ on $\sqrt{E}$ had a very singular character. The graph representing this dependence (Fig. 3) consists of two intersecting straight lines. In the range of values of E from 0 to 3400 V/cm, Frenkel's relation remains valid and is reflected in a straight line with an angle of slope whose tangent is 0.46. On passing this limit in the value of E, however, the straight line abruptly changes direction and its angular coefficient becomes so small that σ ceases to increase with further intensification of the electric field. This turning point is evidently due to electrolytic (high-potential) polarization of the dielectric, since in the present case with a field potential greater than 3400 V/cm, we must regard E not as the applied field but as the effective field, equal to $\frac{V-P}{d}$, where V is the imposed voltage, P is the e.m.f. of polarization and d is the distance between the electrodes.

SUMMARY

1. The electric conductivity of 0.0078 N solutions of iodine in isooctane and benzene was investigated at electric field potentials ranging from 300 to 40,000 V/cm.

2. Solutions of iodine in isooctane and benzene conduct current better than the original hydrocarbons. The conductivity of the benzene solutions is higher than that of the isooctane solutions. The specific electric conductivity (σ) at E = 7500 V/cm of 0.0078 N benzene solution of iodine is $1.27 \cdot 10^{-11}$ ohm^{-1} cm^{-1}, whereas the σ of the original benzene is $1.28 \cdot 10^{-14}$ ohm^{-1} cm^{-1}; the σ of 0.0078 N solution of iodine in isooctane = $8.57 \cdot 10^{-15}$ ohm^{-1} cm^{-1}, whereas the σ of the original isooctane is less than $8.57 \cdot 10^{-15}$ ohm^{-1} cm^{-1}.

3. The electric conductivity of solutions of iodine in isooctane and benzene increases exponentially with rising electric field potential in accordance with Frenkel's equation which finds its graphical expression in the linear dependence of log σ on $\sqrt{E}$.

In conclusion it is our pleasant duty to acknowledge the valuable advice of Corresponding Member of the Academy of Sciences of the U.S.S.R. Ya. I. Frenkel and also to thank O. A. Shpanskaya for assistance in the experimental work.

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Received February 20, 1951

* See Consultants Bureau translation, p. 1157.

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THE ELECTRIC CONDUCTIVITY OF HYDROCARBON SOLUTIONS OF SATURATED FATTY ACIDS

L. G. Gindin and V. A. Kazakova

Very little has appeared in the literature about the electric conductivity of hydrocarbon solutions of carboxylic acids.

Brühl and Schröder [1], in the course of a study of the properties of camphanic acid, report that a 3.29% benzene solution of the acid and its Na salt "do not exhibit appreciable conductivity".

Matthews [2] found a value of $3 \cdot 10^{-8}$ ohm^{-1} cm^{-1} for the specific electric conductivity of a solution of trichloracetic acid (concentration not stated) in benzene, and for this reason he described the solution as "an excellent insulator."

Rabinovich [3] studied the conductivity of some pure dielectrics and of their nonaqueous solutions and determined inter alia the specific electric conductivity (σ) of benzene solutions (σ of the benzene $\leqslant 7.8 \cdot 10^{-13}$) of palmitic and stearic acids. He found a value at 25° C of $\leqslant 3.7 \cdot 10^{-13}$ for the solutions of both acids at all concentrations up to saturation, i.e., the solutions of these acids conducted electricity twice as badly as the original benzene.

Gokhberg and Glikman [4] in an investigation of the dielectric properties of kerosene attempted to clarify the effect of the acid value on these properties. They acidified kerosene with acetic acid, dehydrated it with calcium chloride and then determined the volt-ampere characteristic of the solutions. According to their data only an increase of acid value to 2000-3000 mg KOH/100 g led to appreciable fall of the specific resistance of kerosene whereas an increase in acidity to about 500 had little effect.

These authors were evidently dealing with inadequately dehydrated solutions, since efficient removal of water cannot be effected with calcium chloride.

This was all the scanty material available on the problem. However, we became particularly interested in obtaining further information on the subject because in our studies of the mechanism of corrosion of metals in dielectrics, especially in hydrocarbon solutions of fatty acids [5-9], we lacked the necessary data for the electric conductivity of such solutions and its dependence on the electric field potential.

In these circumstances we decided to determine the required data.

EXPERIMENTAL

We measured the electric conductivity of isooctane solutions of the first five normal members of the homologous series of fatty acids: Acetic, propionic, butyric, valeric and caproic acids, these being the main objects of our corrosion researches.

The isooctane had d_4^{20} 0.700; b.p. (765 mm) 97-99°.

The constants of the acids are listed in the table.

The conductivity was measured at 20°C in the same apparatus and by the same method as for measurements of the electric conductivity of iodine solutions [10]. Isooctane which had been thoroughly dried over sodium was distilled into the apparatus and tested for nonconductivity. The amount of acid required to form a 0.5 N solution was then dissolved in it, after which the volt-ampere characteristic of the solution was determined. A few milliliters of the solution were then used for accurate determination of the acidity, after which more acid was added to raise the concentration to 0.1 N. The volt-ampere characteristic of this solution was then determined, the concentration was again increased, and the procedure was repeated until the concentration was 1.5 N. After completing the

Constants of the Investigated Fatty Acids

Acid	d_4^{20}	Temperature of boiling at 750 mm Hg (°C)	Temperature of boiling at 28 mm Hg (°C)	Temperature of solidification (°C)	Temperature of melting (°C)	Note
Acetic	1.04926	116.0	–	16.85	–	The butyric acid was chemically pure; the remaining acids were of "limited purity" and specially prepared by IREA.
Propionic	0.99340	141.0	–	-21.7	-21.7	
Butyric	0.9640	161.8	–	–	–	
Valeric	0.93906	186.3	–	- 33.8	-33.8	
Caproic	0.92715	205.0	119.5	- 3.8	- 3.8	

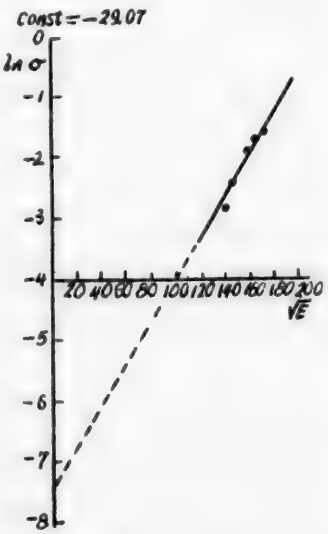
conductivity measurements on one series of solutions, we repeated the operations with a second and third series, and only when the results of measurements in all the three series coincided did they inspire us with confidence in their accuracy.•

Judging by the results of the measurements, isooctane and 0.05-1.5 N solutions therein of caproic, valeric butyric and propionic acids are distinguished by such a low conductivity that it could not be determined with our galvanometer at field potentials of 30 kV/cm. It follows, therefore, that the specific electric conductivity(σ) of the solutions in question is:

$$\leqslant 2.14 \cdot 10^{-15}\ \text{ohm}^{-1}\ \text{cm}^{-1}.$$

The same can be said about 0.05-1.0 N solutions of acetic acid. Concerning the 1.7 N solution of this acid, it exhibited insignificant conductivity in strong fields (at E = 30 kV/cm the value of σ was $3.32 \cdot 10^{-4}$ $\text{ohm}^{-1}\ \text{cm}^{-1}$). This conductivity would probably rise with increasing concentration of solution since the specific electric conductivity of acetic acid itself, according to Rabinovich [3], is a little higher than that of isooctane, namely, $1.12 \cdot 10^{-8}$. In this connection it is highly significant that with increasing electric field strength the conductivity of this solution increases exponentially in accordance with the Frenkel relation [11]:

$$\sigma = \sigma_0 e^{\frac{\sqrt{e^3 E/\epsilon}}{kT}}.$$



Electric conductivity of 1.7 N solution of acetic acid in isooctane.

SUMMARY

1. 0.05-1.0 N isooctane solutions of acetic acid and 0.05-1.5 N solutions of propionic, butyric, valeric and caproic acids are dielectrics. Their specific electric conductivity σ (at E = 30 kV/cm) $\leqslant 2.14 \cdot 10^{-15}$ $\text{ohm}^{-1}\ \text{cm}^{-1}$.

2. The σ of 1.7 N acetic acid in isooctane (at E = 30 kV/cm) is $3.32 \cdot 10^{-14}$ $\text{ohm}^{-1}\ \text{cm}^{-1}$. This solution exhibits exponential increase in conductivity with increasing field strength in conformity with Frenkel's equation.

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Received February 20, 1951

• After the measurements, the solutions were utilized in corrosion tests.

•• See Consultants Bureau English translation, p. 1089.

••• See Consultants Bureau English translation, p. 1806.

OXIDATION OF HYDROCARBON BY ATMOSPHERIC OXYGEN UNDER THE INITIATING ACTION OF CHLORINE

N. I. Zemlyansky, O. A. Prib, and M. Ya. Sharypkina

There is a considerable literature on the theory and practice of oxidation of paraffin hydrocarbons with oxygen of the air, with pure oxygen and with ozone in various conditions with the aim of investigating the possibility of obtaining valuable oxygen-containing intermediate products of oxidation [1]. The formation of oxygen-containing compounds is explained by the well-known theories of Bone [2], Bakh-Engler [3] and N. N. Semenov [4]. In subsequent investigations these theories were analyzed and made more precise, [5] and none of them have been refuted. According to Semenov's theory, oxidation of paraffins involves a chain mechanism [6], and this concept was elaborated by Neiman in the sense that he regarded chain development as being largely dependent upon the free radicals which are formed in the oxidation process [7]. Several workers simultaneously established that the reaction of paraffin hydrocarbons with chlorine involves a chain mechanism [8] and may proceed according to two schemes:

$$Cl_2 \rightarrow 2Cl;$$

(I) $R-H + Cl \rightarrow R + HCl;$ $R + Cl_2 \rightarrow RCl + Cl.$

(II) $R-H + Cl \rightarrow R-Cl + H;$ $H + Cl_2 \rightarrow HCl + Cl.$

It has not up to now been established which mechanism actually applies [9]. One of us obtained data in support of the scheme involving formation of free radicals [10]. If we assume that the interaction of paraffins with chlorine proceeds via free radicals, then chlorine mixed with oxygen must assist the process of hydrocarbon oxidation.

As far back as 1931 it was experimentally established [8] that traces of oxygen inhibit the chlorination of paraffins by forming a chain [11]. There are likewise two possible mechanisms of chain-breaking:

(I) $R + O \rightarrow RO;$ (II) $H + O \rightarrow HO.$

If scheme (I) above for paraffin chlorination is accepted, then chain-breaking will proceed by the first mechanism. With an insufficiency of chlorine and a large excess of oxygen, the chlorine might be expected to function as an initiator of free radical formation and thus facilitate the commencement of oxidation of paraffins by oxygen.

Consequently the initiating action of chlorine on the process of thermal oxidation of paraffins is only possible under the conditions of the first of the above chain-breaking schemes and the first of the above chlorination schemes.

We carried out experiments on the oxidation of methane with atmospheric oxygen in presence of chlorine, using various ratios of reagents and various temperature ranges. The experiments showed that in presence of chlorine the oxidation proceeds at much lower temperatures than in the absence of chlorine. In presence of chlorine the reaction products were found to include formaldehyde, formic acid, CO_2 and hydrogen chloride. In preliminary experiments on oxidation of methane with oxygen in presence of chlorine at normal pressure the presence of methyl alcohol was detected; this is normally formed by methane oxidation only under pressure. We are inclined to the opinion that these experimental data support the free-radical mechanism and also the chain-breaking mechanism (I). We also believe we have obtained a theoretical explanation of the catalytic action of chlorine and other halogens on the processes of oxidation of paraffin hydrocarbons previously reported in some patents. In our view the initiating action of chlorine on thermal oxidation of paraffin hydrocarbons proceeds by the following scheme:

$$CH_4 + Cl \rightarrow CH_3 + HCl;$$
$$CH_3 + O_2 \rightarrow CH_3-O-O^{\cdot};$$
$$CH_3-O-O^{\cdot} + HCl \rightarrow CH_3-O-OH + Cl;$$
$$CH_3-O-O-H \rightarrow CH_2O + H_2O.$$

EXPERIMENTAL

We used natural gas from the Dashau field in the Lvov region with the following composition: Methane 98.39%, higher homologs 0.55%, oxygen and nitrogen 0.01%. The chlorine was commercial gas in cylinders and was not analyzed. Air was introduced with a pump. Oxidation was performed in the apparatus here illustrated.

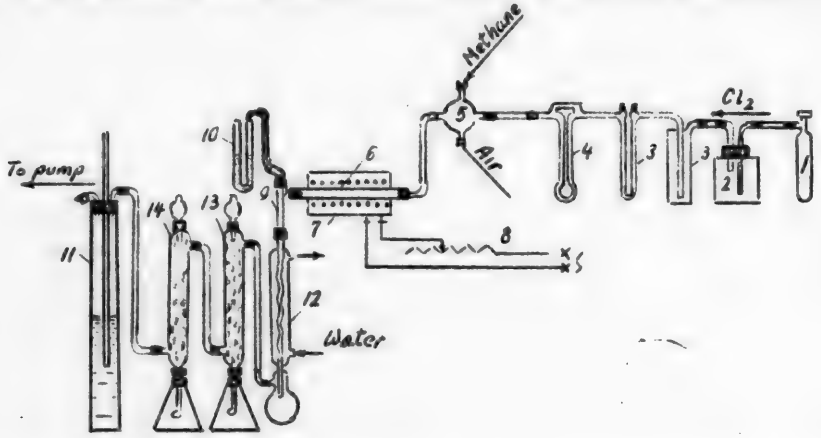

Diagram of apparatus for oxidation of methane with atmospheric oxygen in presence of chlorine.

Only the set-up for the chlorine supply is shown in the diagram since the method for feeding methane and air was the same. Gas from cylinder 1 entered the gas-purifying bottle 2. The chlorine was purified by passing through water and the methane and air were washed with 30% potassium hydroxide.

Each gas was separately dried with concentrated sulfuric acid 3 and with calcium chloride; it then passed through the flowmeter 4 and entered the glass mixer 5 whose sides were blackened. The gas mixture entered the porcelain tube 6 (diameter 1.5 cm) which was heated by the electric furnace 7. The temperature was regulated by the rheostat 8. By means of the three-way connection 9 the porcelain tube was connected with the open manometer 10 and the vertical condenser 12 to which was attached a receiver. Through a glass tube the receiver was joined to two absorption columns (in series) 13 and 14. The columns were 0.5 meter high and filled with glass rings. Distilled water trickled down the first column and standard solution of potassium hydroxide down the second. The second receiver was connected to the manostat 11 for maintenance of normal pressure in the apparatus. Withdrawal of samples of gases was effected by attaching a gasometer to the porcelain tube 6 for a definite period of time. The following components were determined in the liquid in the receivers: methyl alcohol, by formation of methyl salicylate (qualitatively); formaldehyde in the first and second receivers was determined by the method of Molotkova and Zolotukhin [12]; organic acids were determined by the difference between the total acidity, and the acidity due to hydrochloric acid (Folgard method); free chlorine was determined iodometrically; CO_2 was determined by the Winkler method [13]. A sample of the gases was analyzed in a VTI apparatus for its content of CO_2, CO, unsaturated hydrocarbons and oxygen. The amounts of methane and chlorine used in an experiment were determined. There is no information in the literature about the temperature at which methane is oxidized when passed in admixture with air through a heated tube without a catalyst. In order to determine the initiating action of chlorine on the oxidation, we carried out two experiments on oxidation of methane with oxygen of the air without chlorine by passing a methane-air mixture (ratio 1:4) at 350° and a contact time of 0.11 minute through our apparatus. The duration of the first of these experiments was 5 hours, and that of the second was 10 hours. In these conditions the methane did not react with appreciable speed with atmospheric oxygen, for even after 10 hours no products of methane oxidation could be detected. Oxidation of methane with atmospheric oxygen in presence of chlorine was performed in two series of experiments (experiments 1-5 and 6-10). The duration of each experiment was 20 hours and was conducted in two parallel apparatuses. Mean results of the experiments are presented in the table.

The data show that at a contact time of 0.11 minute methane reacts with atmospheric oxygen even at a temperature of 350°. The yield of formic acid, formaldehyde and CO_2 increases with rising temperature from 350°

Results of Oxidation of Methane with Atmospheric Oxygen in Presence of Chlorine

No. of expt.	Volume ratios methane: air: chlorine	Period of contact (minutes)	Temp.	Content of products after reaction (in %)						% of methane reacted
				Methyl alcohol	Formaldehyde	Formic acid	CO_2	Chlorine as HCl	Free chlorine	
1	12:36:1	0.11	350°	–	0.08	0.2	0.12	16.6	30.47	0.4
2	12:36:1	0.11	500	–	0.13	0.14	0.65	54.34	None	0.92
3	12:36:1	0.11	600	–	0.16	0.94	0.68	51.87	–	1.78
4	12:36:1	0.11	800	–	0.27	1.05	1.26	94.77	–	2.58
5	12:36:1	0.04	600	–	0.36	None	0.37	41.48	15.80	0.73
6	12:37:0.006	0.22	350	–	0.059	0.16	–	33.82	57.30	0.219
7	12:37:0.006	0.22	500	–	0.054	0.16	–	72.0	26.75	0.214
8	12:37:0.006	0.22	600	–	0.065	0.14	–	94.0	None	0.205
9	12:37:0.006	0.22	800	–	0.265	0.35	–	88.1	None	0.615
10	12:37:0.006	0.13	500	–	0.058	0.14	8.09	51.35	41.62	8.20

to 800°. The increase in the formaldehyde yield is proportional to the temperature rise. Comparing the first with the second series, we see that a drop in the amount of chlorine lowers the formaldehyde yield. A fall in the duration of contact with the heated surface in the first series leads to an increased formaldehyde yield. The yield of formic acid increased in the first series with rising temperature at a contact period of 0.11, but it fell off sharply and became zero at a contact time of 0.04 minute. In the second series of experiments the yields of formic acid changed to an insignificant extent with rising temperature. Up to 600° in the first series of experiments the chlorine enters into a chlorination reaction as indicated by the amount of chlorine found as HCl. At 350° the chlorine not entering into reaction is recovered. At 800° the greater part of the chlorine is converted into hydrogen chloride which results in an increase in the yields of all the oxidation products (experiment 4). A fall in the contact time to 0.04 minute led to the appearance of unreacted chlorine (experiment 5), probably because for technical reasons we had to reduce the volume of the porcelain tube by packing with lumps of porcelain in order to reduce the time of contact. The same factor was responsible for the sharp drop in CO_2 yield in the second series with falling contact time and for the rise in the amount of unreacted chlorine.

The data justify the claim that chlorine initiates the chain reaction of oxidation of methane with atmospheric oxygen.

SUMMARY

The initiating action of chlorine on the oxidation of methane (natural gas) with atmospheric oxygen was investigated. The oxidation proceeds at lower temperatures in presence of chlorine than in its absence. Change of the contact time and of the amount of chlorine in the reaction mixture leads to change in the amount of oxidation products. Yields of formaldehyde and formic acid in presence of chlorine were much higher than in its absence in the same conditions. A reaction mechanism involving free-radical formation is confirmed by the experimental data.

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Received May 22, 1951

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REARRANGEMENT OF HYDROGEN IN OLEFINIC HYDROCARBONS OVER ALUMINOSILICATE CATALYSTS

A. A. Petrov and A. V. Frost *

Formation of saturated hydrocarbons from olefins under the action of aluminosilicates (floridin) was first observed by S. V. Lebedev [1] in studies of the depolymerization of diisobutene and diisoamylene. Subsequently the very complex process was closely studied, although over another catalyst, by S.S. Nametkin and co-workers [2]. This process, proceeding under the action of sulfuric acid and known as "hydrodehydropolymerization", generally takes place with rearrangement of hydrogen when carried out in presence of aluminosilicates. In contrast to what happens over aluminosilicates, however, the formation of saturated products in presence of sulfuric acid is only observed in the polymer fractions. The process of hydrogen rearrangement over aluminosilicates was closely investigated by A.V. Frost and co-workers [3]. Of investigations by foreign authors we may draw attention to the work of Thomas [4] who showed that carbonaceous deposits on the catalyst play an important part in the hydrogen rearrangement.

The present investigation is mainly concerned with the dependence of hydrogen rearrangement on the structure of the original hydrocarbon. A study is also made of the effect of such factors as space velocity and amount of catalyst on the yield of saturated products. The experimental conditions excluded cracking in order, as far as possible, to obtain an accurate hydrogen balance after hydrogen rearrangement alone, and also to obtain some insight into the mechanism of the catalytic processes.

In previous researches [5] we showed that olefins with a tertiary double bond are more susceptible to saturation than olefins with a primary-secondary double bond. In this paper we report on a more comprehensive investigation of the saturation of both olefins and cycloolefins with various structures and molecular weights. Results are summarized in Table 1.

TABLE 1

Experimental Conditions: Space Velocity 0.2 l/hour; Ratio of Volumes of Catalyst and Starting Material 3:1; Duration of Experiment 100 Minutes

Initial hydrocarbon	% yield of saturated hydrocarbons	Initial hydrocarbon	% yield of saturated hydrocarbons
Hexene-1	33.7	Octene-1	38
3-Methylpentene-3	44.7	4-Methylheptene-4	51.5
2-Methylpentene-2	50.0	2-Ethylhexene-1	54.5
2,3-Dimethylbutene-2	39.5	3-Ethylhexene-2	54.6
2,2-Dimethylbutene-3	35.3	Nonene-1	62.2
Heptene-1	36.8	Nonene-4	50.6
Heptene-3	34.4	Decene-1	84.5
3-Methylhexene-2	58.4	4-Propylheptene-4	67.9
2-Methylhexene-2	62.0	5-Methylnonene-5	75
2,4-Dimethylpentene-2	41.9	Cyclohexene	99.7
5-Methylhexene-1	53.1	1-Methylcyclopentene-1	99.8

In view of the fact that the cycloolefins underwent much more saturation than the olefins, an examination of the effect of the structure of the initial cyclic hydrocarbon on the yield of saturated products was made under somewhat different conditions: Space velocity 0.6 l/hour; ratio of catalyst to raw material volume 1:1: duration of experiment 100 minutes. Results for saturation of the cycloolefins are given in Table 2.

Before discussing the data of Tables 1 and 2, we propose to consider the mechanism of the catalytic processes. The first question which presents itself is: What is the source of hydrogen for the saturation? The catalyzate from any hydrocarbon consisted of a fraction whose boiling point corresponded to isomers of the initial hydrocarbon

* Deceased.

together with a higher boiling fraction presumably made up of polymers of the original hydrocarbon.

In none of the experiments did the monomer fraction contain products with a lower hydrogen content (aromatics, diene hydrocarbons, etc.) than in the original hydrocarbons. Consequently no reactions took place of the type of Zelinsky's irreversible catalysis on aluminosilicates and the hydrogen did not originate from the monomer fraction. The polymer fraction, especially in the experiments with olefins, had a very wide boiling range. A small proportion of aromatic hydrocarbons was found in the higher boiling portions (Table 3). This table also reveals, however, that the main constituents of the polymer fractions were the same saturated products as were found in the monomer fraction; the small aromatic content of the higher boiling fractions is most probably, as will be shown later, the result of secondary processes.

TABLE 2

Initial hydrocarbon	% yield of saturated hydrocarbons
Cyclohexene	46
1-Methylcyclohexene-1	61
1-Methylcyclohexene-3	57
1-Propylcyclohexene-1	57
Allylcyclohexene	60
1-Methylcyclopentene-1	74
1-Butylcyclopentene-1	71
Hexene-1 (for comparison)	8

Moreover the results of combustion of the polymer fractions from the experiments with hexene-1 and cyclohexene showed that these fractions yield a total of only 9% of the hydrogen required for saturation of the monomer fractions in the olefin experiments and 16% of the hydrogen needed in the cycloolefin experiments. It is thus quite clear that the main hydrogen source for saturation of olefinic hydrocarbon by hydrogen rearrangement is the formation of products of condensation over the catalyst (coke). Indeed, the formation of coke on the catalyst is in direct relation to the amount of saturated hydrocarbons formed in an experiment. On the average (from experiments with 25 different hydrocarbons) 0.45-0.52 g coke on the catalyst corresponds to each gram of saturated hydrocarbons formed. Which factors influence coke formation and, in turn, the formation of saturated hydrocarbons?

TABLE 3

Composition of Polymer Fraction of Experiments with Hexene-1 *

B.p.	Yield (in %) of starting material	Yield (in %) of polymers	n_D^{20}	% olefins	Per cent H	Per cent C	Sulfonatable
80-100°	1.6	5.7	1.4030	68	14.55	–	–
100-150	3.1	17.8	1.4090	72	14.55	84.13	–
150-200	7.0	39.5	1.4376	65	14.19	85.06	56
200-250	3.4	19.6	1.4584	51	13.85	86.37	61
250-300	2.6	15.2	1.4916	27	12.84	87.18	74
above 300	0.3	2.0	–	–	–	–	–

In a preceding investigation on octenes we showed that the saturated hydrocarbons yield is closely related to the catalyst: starting material ratio (by volume). This is also supported by the data of Figure 1.

The amount of coke formed in these experiments is also closely dependent upon the catalyst amount, as shown in Fig. 2.

Inspection of Figures 1 and 2 clearly shows the relation between coke formation and amount of saturated hydrocarbons, and the relation between coke formation and amount of catalyst. We can infer from these diagrams that the absolute amount of coke formed per unit volume of catalyst is wholly dependent on the nature of the starting material.

The process of coke formation (and in turn of saturated

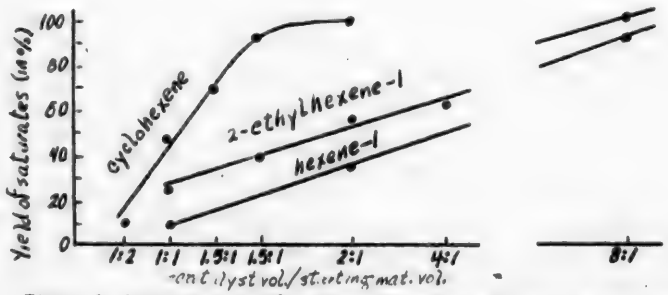

Figure 1. Saturation as a function of the catalyst volume (each experiment was performed with 50 ml hydrocarbons).

* The monomer fraction of these experiments contained 60% olefins and had n_D^{20} 1.3877. The initial substance (hexene-1) contained 14.24% hydrogen and 85.76% carbon.

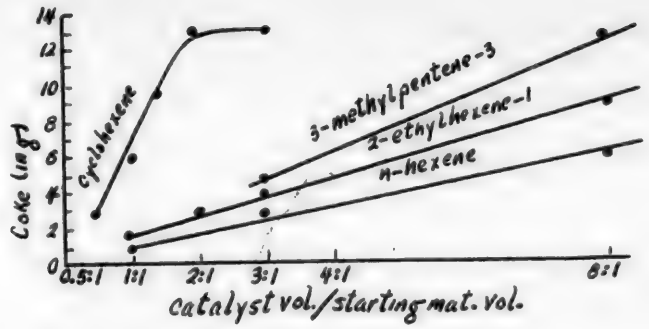

Fig. 2. Effect of amount of catalyst on coke formation

hydrocarbons formation) may thus be said to involve, firstly, formation of a certain amount of polymers (dimers and trimers) of the original hydrocarbon. Assuming the aluminosilicate to be in the form $(HAlSiO_4)_x$ (HA for short) – i.e., a compound with the properties of an inorganic acid and capable of exchanging hydrogen atoms with hydrogen atoms of the reacting hydrocarbon– then polymerization (say of hexene-1) might proceed as follows:

$$CH_2=CH-R + HA \rightarrow CH_3-CHA-R \quad (I)$$

$$CH_3-CHA-R + CH_2=CH-R \longrightarrow$$

$$\longrightarrow R-\underset{\displaystyle CH_3}{CH}-CH=CH-R + HA,$$

i.e. entirely in analogy with the Butlerov scheme for polymerization of olefins in presence of sulfuric acid.

A molecule of formed dimer can react afresh with catalyst:

$$R-\underset{\displaystyle CH_3}{CH}-CH=CH-R + HA \rightarrow R-\underset{\displaystyle CH_3}{CH}-CHA-CH_2-R \quad (II)$$

We can now suggest that reaction occurs between the complexes (II) (polymer molecules combined with catalyst) and (I) (monomer molecules combined with catalyst) to give molecules of paraffin hydrocarbon and of a complex (III) with a lower hydrogen content:

$$R-\underset{\displaystyle CH_3}{CH}-CHA-CH_2-R \rightarrow R-\underset{\displaystyle CH_3}{CH}-CHA-CHA-R \quad (III)$$

$$CH_3-CHA-R \rightarrow CH_3-CH_2-R$$

The process can later be repeated with formation of a fresh molecule of paraffin hydrocarbon and of a polymer-aluminosilicate complex (IV) still poorer in hydrogen:

$$R-\underset{\displaystyle CH_3}{CH}-CHA-CHA-CHA-R \quad (IV)$$

On the average each polymer molecule can give 3-4 hydrogen molecules for the saturation of the monomer fraction. A series of data confirming this may be adduced. The deposits on the catalyst, according to Thomas [4], have the empirical formula $CH_{1.3}$. According to our determinations the elementary composition of the coke (C 91%, H 9%) corresponds to the empirical formula C_nH_{2n-3} (styrene type). The above conclusion that 1 g of formed saturated hydrocarbon corresponds to 0.45-0.52 g coke on catalyst is also in good agreement with the assumption that each polymer molecule yields 3-4 molecules of hydrogen for saturation.

It must be emphasized that the so-called coke contains a high proportion of hydrogen and that the name is purely arbitrary.

After releasing 3-4 molecules of hydrogen a small amount of the polymers may be desorbed (strictly speaking, detached from the catalyst) to form the aromatic hydrocarbons found in the catalyzate.

Support for the above mechanism of hydrogen rearrangement is also obtained in our studies of the dynamics of the processes taking place on the catalyst. By dynamic processes we understand the part played by individual transformations (isomerization, polymerization, yield of saturated hydrocarbons, yield of aromatic hydrocarbons) in the separate stages of an experiment. We carried out an investigation along these lines by spacing out an experiment for a period of 5 hours (instead of 100 minutes) and taking samples and investigating the products of transformation of each individual stage. The results of these investigations are as follows: During the first 40-60 minutes intensive saturation and isomerization occur, also much coke formation; products poor in hydrogen are absent from the polymers.

After 60 minutes coke formation terminates and formation of saturated products is insignificant and usually ceases after 80-100 minutes.

The most interesting feature is that aromatic hydrocarbons appear in the catalyzate (although, as already noted, only in the polymer fractions) only after a sharp drop in formation of saturated products, namely, after 60-80 minutes of catalyst operation. The fresh catalyst, most active for hydrogen rearrangement, did not give liquid aromatic hydrocarbons. The latter only appeared in the catalyzate after a certain period of operation of the catalyst which was already incapable of catalyzing hydrogen rearrangement reactions. We are thus justified in assuming that the appearance of small amounts of aromatic hydrocarbons in the catalyzates is the consequence of secondary reactions.

Let us revert now to the data of Tables 1 and 2. The more intensive saturation of olefins containing tertiary double bonds is evidently explained by the greater ease of polymerization of such hydrocarbons. According to Lebedev [6], for instance, only tetrasubstituted and asymmetrically disubstituted ethylene derivatives undergo polymerization over floridin. But symmetrically disubstituted, monosubstituted and tetrasubstituted olefins, according to Lebedev, do not polymerize over floridin. This accounts for the less intensive saturation of hexene-1 in comparison say, with 2-methylpentene-2, since the first stage of the hydrogen rearrangement process (polymerization) must be preceded by isomerization of the first hydrocarbon into the second.

The increase of yield of saturated products with increasing molecular weight of the initial hydrocarbon can be accounted for by the different properties of the polymers formed. Whereas the primary product of hexene polymerization (dodecene) is a gas under the experimental conditions and is relatively easily desorbed from the catalyst surface, decene dimer is bound to be tenaciously chemisorbed and precipitated on the catalyst. The intensified saturation of cycloolefins is directly related to their intensified polymerization. For example, in identical conditions, hexene-1 and cyclohexene yield respectively 17% and 28% polymers. Taking into consideration the same large difference in degree of coke formation (respectively 11% and 31%), then the more intensive polymerization of cycloolefins in comparison with open-chain olefins is obvious. We may add that the ease of catalytic transformations of cycloolefins does not apply only to polymerizations and hydrogen rearrangements; cycloolefins also undergo isomerization much more readily.

It is interesting to note that in the case of cycloolefins the yield of saturates did not increase with increasing molecular weight of the initial hydrocarbon. This is because the increase in molecular weight of cycloolefins was due to introduction of an aliphatic radical into the ring, and this naturally accentuated the olefinic as distinct from the ring structure

The process of hydrogen rearrangement is notable for the formation of saturated hydrocarbons containing a tertiary carbon atom, pointing to selective saturation of olefins with a tertiary double bond. Such a specific effect on the tertiary double bond is only exercised by aluminosilicates, since the numerous investigations of Lebedev [7] indicate that in normal hydrogenation conditions, using molecular hydrogen, monosubstituted olefins are saturated more intensively. Selective saturation of olefins containing tertiary double bonds plays an important part in the accumulation of branched hydrocarbons in the products of catalytic cracking. Thus the tertiary olefins formed by isomerization are rapidly saturated and thereby removed from the processes taking place at the catalyst.

EXPERIMENTAL

The study of the hydrogen rearrangement processes was carried out in an ordinary apparatus for the investigation of catalytic processes in a flow system. All the experiments were performed at 250°. The cracking experiments (octene-1) were performed in the same conditions but starting at 350°. The catalyst was a synthetic aluminosilicate cracking catalyst of the Houdry type. The conversion products consisted of liquid catalyzate (70-90% yield) and coke on the catalyst (10-30% yield). The coke was determined by weighing the catalyst before and after the experiment. The catalyzate was fractionally distilled to give the monomer of the original hydrocarbon (yield 50-80%) and higher boiling (polymer) fraction (10-30% yield). The amount of saturated products formed in the hydrogen rearrangement reaction was calculated on the basis of the bromine number of the monomer fraction. In each experiment 50 ml hydrocarbon was taken.

Aromatic hydrocarbons were determined by sulfonation with 100% sulfuric acid. The structural investigation of the formed saturated hydrocarbons is described in another paper and will therefore not be considered here.

In Table 4 are presented some data for the catalyzates. Experimental conditions were the same as in Table 1 and 2.

TABLE 4

Initial hydrocarbon	Yield (% of raw material)			Monomer n_D^{20}	Polymer n_D^{20}
	Monomer	Polymer	Coke		
Hexene-1	63	18	11	1.3877	1.4446
3-Methylpentene-3	63	16	14	–	–
2-Methylpentene-2	59	–	14	1.3815	1.4470
2,2-Dimethylbutene-3	57	16	11	1.3928	1.4430
Heptene-1	68	15	11	1.3980	1.4480
Heptene-3	65	–	12	1.3975	1.4455
Octene-1	63	13	–	1.4070	1.4560
3-Ethylhexene-3	63	12	15	1.4020	1.4565
Decene-1	43	8	34	–	–
Cyclohexene	50	30	15	1.4263	1.5012
1-Methylcyclohexene-1	57	22	–	1.4315	1.5050
1-Methylcyclohexene-3	57	20	–	1.4335	1.4960
1-Methylcyclopentene-1	40	40	12	1.4155	1.5015
1-Butylcyclopentene-1	57	13	–	1.4390	1.4960

All the hydrocarbons utilized in the research were usually obtained by dehydration of the corresponding alcohols. Primary and secondary alcohols were dehydrated over alumina, the primary ones at 375° and the secdary at 325°. Tertiary alcohols were dehydrated by slow distillation with iodine. 1-Alkenes were prepared from primary normal alcohols. They may possibly contain small amounts of 2-alkenes. 2-Methylpentene-2 was prepared from dimethylpropyl carbinol synthesized by a Grignard reaction from acetone and propyl magnesium bromide. 3-Methylpentene-3 was prepared from diethylmethyl carbinol (from methylethyl ketone and ethyl magnesium bromide). 2,3-Dimethylbutene-2 was prepared from dimethylisopropyl carbinol (from methylisobutyrate and methyl magnesium iodide). Heptene-3 and nonene-4 were prepared from the dialkyl carbinols synthesized from methyl formate and the corresponding alkyl magnesium bromides. 2-Methylpentene-2 was prepared from dimethylbutyl carbinol. This alcohol was derived from acetone and butyl magnesium bromide. 3-Methylpentene-3 was prepared from methylethylpropyl carbinol (from methylethyl ketone and propyl magnesium bromide). 2,4-Dimethylpentene-2 was obtained by dehydration of diisopropyl carbinol prepared by catalytic reduction of diisopropyl ketone. 2-Ethylhexene-1 was prepared from 2-ethylhexanol-1. 3-Ethylhexene-3 was prepared from diethylpropyl carbinol (from ethyl butyrate and ethyl magnesium bromide). 4-Methylheptene-3 was prepared from dipropylmethyl carbinol (from ethyl acetate and propyl magnesium bromide). 4-Propylheptene-3 was prepared from tripropyl carbinol (from ethyl butyrate and propyl magnesium bromide). 5-Methylnonene-4 was prepared from dibutylmethyl carbinol (from ethyl acetate and butyl magnesium bromide). Cyclohexene was prepared from cyclohexanol; 1-methylcyclohexene-1 from 1-methylcyclohexanol-1 (from cyclohexanone and methyl magnesium iodide); 1-methylcyclohexene-3 from hexahydro-p-cresol: 1-propylcyclohexene-1 from 1-propylcyclohexanol-1 (from cyclohexanol and propyl magnesium bromide). 1-Methylcyclopentene-1 was prepared from 1-methylcyclopentanol-1 (from cyclopentanone and methyl magnesium iodide). 1-Butylcyclopentene-1 was prepared from 1-butylcyclopentanol-1 (from cyclopentanone and butyl magnesium bromide). 5-Methylhexene and allylcyclohexane were got by condensation of the corresponding alkyl halides with allyl bromide (Grignard-Wurtz reaction).

The constants of the hydrocarbons (after purification in the usual manner by repeated fractionation over sodium and also in a column of ten theoretical plates) are presented in Table 5. (See next page)

The 1-alkenes may contain small amounts of 2-alkenes.

The data of Table 5 are in good agreement with those in the handbooks of Egloff [8] and Obolentsev[9].

SUMMARY

1. Hydrogen rearrangement in olefins over aluminosilicate in conditions excluding cracking was investigated.

2. Cyclic olefins are found to be more intensively saturated than open-chain olefins.

3. A mechanism is advanced for the formation of saturated hydrocarbons which involves transfer of hydrogen by the condensation products to the catalyst. The condensation products formed are probably polymers of the original hydrocarbon.

4. It is shown that the amount of saturated hydrocarbons formed is in direct relation to the amount of coke on the catalyst.

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TABLE 3

Hydrocarbon	B.p.	n_D^{20}	d_4^{20}	Bromine no.
Hexene-1	63-68	1.3900	0.6749	191
3-Methylpentene-3	68-69	1.4026	0.6952	190
2-Methylpentene-2	65-66	1.3965	0.6870	193
2,3-Dimethylbutene-2	70-72	1.4087	0.7108	177
2,2-Dimethylbutene-3	41-43	1.3765	0.6556	192
Heptene-1	93-94	1.4010	0.6982	162
Heptene-3	95-96	1.4030	0.7014	159
2-Methylhexene-2	94-95	1.4038	0.7120	157
3-Methylhexene-2	93-95	1.4105	0.7159	164
5-Methylhexene-1	84-85	1.3965	0.6926	165
2,4-Dimethylpentene-2	79-82	1.4010	0.6960	162
Octene-1	121-123	1.4122	0.7182	142
2-Ethylhexene-1	119-120	1.4168	0.7300	137
3-Ethylhexene-2	119-120	1.4205	0.7310	150
4-Methylpentene-3	118-120	1.4164	0.7306	142
Nonene-1	146-147	1.4167	0.7278	125
Nonene-4	145-146	1.4175	0.7308	125
Decene-1	171-172	1.4217	0.7421	113
5-Methylnonene-4	165-166	1.4286	0.7498	114
4-Propylheptene-3	156-158	1.4277	0.7598	114
Cyclohexene	82.5-83	1.4443	0.8109	196
1-Methylcyclohexene-1	110-111	1.4502	0.8147	163
1-Methylcyclohexene-3	102-103	1.4420	0.7998	167
1-Propylcyclohexene-1	150-152	1.4580	0.8410	110
1-Methylcyclopentene-1	75-76	1.4270	0.7761	194
Allylcyclohexene	148-151	1.4507	0.8088	118
1-Butylcyclopentene-1	155-157	1.4490	0.8110	142

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Received May 11, 1951

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REACTION OF BORON FLUORIDE ETHERATE WITH ORGANIC CARBOXYLIC ACIDS AND PHENOL

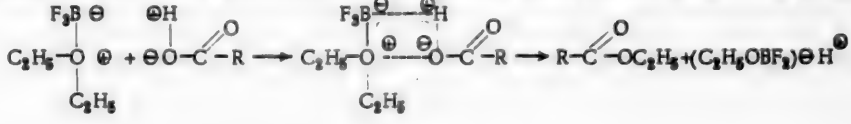
S. V. Zavgorodny

In textbooks of organic chemistry dialkyl ethers are usually described as very stable compounds [1] with low reactivity [2] and very difficult to bring into reaction [3]. At the present time this evaluation is inconsistent with what we know of compounds of this class. Dialkyl ethers are relatively reactive and in certain conditions enter into reaction with the most diverse reagents. Apart, for instance, from the well-known reactions with hydrogen halides, metallic sodium and organometallic compounds, they can be cleaved by organic carboxylic acids [4] and their anhydrides [5] and by acid chlorides [6] in presence of boron fluoride as catalyst.

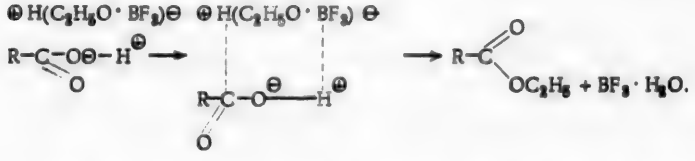
As far back as 1935-1936 [7], in a study of the addition of organic halo-substituted acids to olefins in presence of boron fluoride etherate, we noted that when this catalyst was employed in considerable amounts and the reaction proceeded for a long period at 100° very small amounts of ester-like products were formed which boiled at lower temperatures than the anticipated butyl or amyl esters of the acids. But at the time we did not concern ourselves with these products and they remained uninvestigated. In this paper we deal specially with the reaction of boron fluoride etherate with acetic, chloracetic and, bromacetic acids and with phenol, and we find that in the form of its complex with boron fluoride, diethyl ether is cleaved by the specified acids and by phenol to form the corresponding esters.

The probable reaction mechanism involves activation of the acid molecule by the initial dipole complex of boron fluoride with ether and the formation of a ternary complex in which both the ether and the acid possess heightened reactivity. Heat treatment results in cleavage of this complex into ester and boron fluoride-ethyl alcohol compound (scheme I). In certain conditions these may be the final products. When acid is present, however, it may happen that the very reactive compound of boron fluoride with ethyl alcohol will react further with the acid to form the ternary complex which then breaks down to ester and boron fluoride monohydrate (scheme II).

(I)



(II)



Thus one mole of ether may convert two moles of acid into ester. It must be remembered, however, that the reaction is more complex in practice than is represented by the two above schemes. Deposition on the test tube walls, above the layer of reaction mixture, of a white solid of inorganic origin, especially in experiments with prolonged heating at over 100°, is due to the action of hydrogen fluoride (possibly formed by decomposition of the boron fluoride-ethyl alcohol compound in accordance with the reaction $C_2H_5OH \cdot BF_3 \longrightarrow C_2H_5OBF_2 + HF$ [9].). The degree of cleavage depends on the acid and increases in the order acetic-chloracetic-bromacetic. For example, on heating a 1:2 mixture of boron fluoride etherate and acetic acid for 20 hours on the boiling water bath, ethyl acetate is obtained in 21% yield. In similar conditions the ethyl ester of chloracetic acid is formed in 32% yield. On heating boron fluoride etherate with bromacetic acid in a ratio of 1:2 for 6 hours on an oil bath at 135-145°, the ethyl ester of bromacetic acid is obtained in 52% yield. Apart from its theoretical interest, the reaction here described may find practical application for ester syntheses.

EXPERIMENTAL

Preparation of ethyl acetate. Into a broad test tube is introduced glacial acetic acid and boron fluoride etherate. The mixture formed a light-brown transparent liquid. The test tube was closed with a rubber stopper and heated for 20 hours on the boiling water bath. The mixture turned almost black and opaque. After cooling, the test tube was opened and did not exhibit appreciable gas pressure. The reaction mixture was treated with 8% sodium hydroxide solution. The ester was separated, washed with water, dried with calcium chloride and distilled to give a colorless liquid with a pleasant odor. After a second distillation it had b.p. 76-78°; d_4^{18} 0.9023. 6.8 g acetic acid and 7.32 g boron fluoride etherate gave 1.47 g ethyl acetate or 21.3% (14.7% of the theoretical yield.*

Preparation of ethyl ester of monochloracetic acid. A mixture of 0.05 mole of chemically pure chloracetic acid and 0.05 mole boron fluoride etherate was heated for 20 hours on the water bath. No crystals separated after standing overnight and the mass remained in the form of a homogeneous dark-brown liquid. On opening the tube the liquid fumed and had a weak lachrymatory action. The product was worked up as before, dried with calcium chloride and distilled at atmospheric pressure. A few drops of ethyl ether came over up to 40°, after which the temperature rose quickly to 142° and the whole of the ester distilled as a colorless liquid at 144-146°; n_D^{14} 1.4280; d_{14}^{14} 1.1631. 7.82 g boron fluoride etherate and 9.5 chloracetic acid gave 2.95 g of ethyl ester of chloracetic acid or 31.8% (21.7%) of the theoretical yield.

Preparation of ethyl ester of bromacetic acid. The heterogeneous mixture of bromacetic acid (prepared by Higginbottom's method [8]) and boron fluoride etherate was heated for 6 hours on the oil bath at 135-145°. The mass was black and opaque. In the upper part of the reaction tube was formed a dense layer of white inorganic material. A slight detonation occurred when the tube was opened. The reaction mixture was worked up as before. The ester was a colorless, very lachrymatory, heavy liquid and distilled at atmospheric pressure at 164-169°. From 4.62 g boron fluoride etherate and 8.1 g bromacetic acid was obtained 3.62 g ethyl ester of bromacetic acid or 52.00% (34.4%) of the theoretical yield.

After a second distillation the ester had b.p. 167-168.5°, n_D^{14} 1.455; d_{14}^{14} 1.5134.

Preparation of phenetole. As in the experiments with acids, 4.92 g phenol and 3.46 g boron fluoride etherate were charged into a wide test tube. The phenol dissolved readily after brief shaking and the homogeneous liquid (tube stoppered) was heated for 12 hours on the boiling water bath. The mixture was then diluted with 8% sodium hydroxide solution and the ethereal product of the upper layer was treated with alkali solution until a drop of it on a watch glass no longer gave a turbidity with hydrochloric acid. The product was then washed with water, dried with potassium carbonate and distilled at atmospheric pressure. There was obtained 1.38 g phenetole with b.p. 170-172° or 33.6% of the theoretical amount calculated on the ether.

Performance of the reaction at 135-150° leads to formation of a complex mixture of products boiling at 230-275°.

SUMMARY

1. The reaction of boron fluoride etherate with acetic, chloracetic and bromacetic acids and phenol has been investigated.

2. The possibility of synthesis of alkyl phenol ethers and of esters of carboxylic acids from ethers in presence of boron fluoride has been established.

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Received April 22, 1951

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* In all the later experiments the yield of esters is calculated on the ethyl ether according to scheme I (first number) and scheme II (value in brackets) or on the basis of the total amount of ether and acid used in the reaction.

SYNTHESIS OF ORGANOELEMENT COMPOUNDS OF THE ALIPHATIC SERIES BY THE DIAZO METHOD

III. SYNTHESIS OF COMPOUNDS OF GROUP IV ELEMENTS – ORGANOSILICON COMPOUNDS

A. Ya. Yakubovich and V. A. Ginsburg

Aliphatic diazo compounds can be successfully used, as we have shown, for the preparation of organic compounds of group V elements [1].

In the present communication we present the results of application of the diazo method to the synthesis of organoelement compounds of silicon – an element of the fourth group of Mendeleev's periodic system [2].

At the ordinary temperature silicon tetrachloride energetically, and sometimes explosively, decomposes diazomethane with evolution of nitrogen and formation of a solid, silicon-free product of polymerization of methylene radicals known as "polymethylene". But if the reaction is carried out at –55-45°, then polymethylene is not formed, or only formed to a limited extent, and the reaction products are organosilicon compounds which are obtained in 65-75% yields:

$$SiCl_4 + CH_2N_2 \longrightarrow ClCH_2SiCl_3 + N_2$$

$$ClCH_2SiCl_3 + CH_2N_2 \longrightarrow (ClCH_2)_2SiCl_2 + N_2 \text{ etc.}$$

It is easiest to effect introduction of one methylene group into the $SiCl_4$ molecule with formation of chlormethyltrichlorsilane. Introduction of second and further groups proceed with progressively increasing difficulty. Even more difficult is the methylenation of unsubstituted alkylchlorsilanes such as methyltrichlorsilane; the latter is formed with diazomethane with a small yield of chlormethyldichlormethylsilane. Trialkylchlorsilanes, for example triethylchlorsilane, are not methylenated at all by diazomethane. Diazoethane reacts in a similar manner to diazomethane but more energetically.

There is observed a correlation between the fall in yields of organosilicon compounds with increasing substitution of the chlorine in $SiCl_4$ by aliphatic radicals and the speed of decomposition of diazo compounds under the action of organosilicon halides, the speed falling sharply in the same sequence. In the case, for instance, of triethylchlorsilane, diazo compounds are decomposed with extraordinary slowness, and apparently only in presence of moisture in the diazomethane solution which hydrolyzes the silicon chloride. But even alkyltrichlorsilanes, for example CH_3SiCl_3, react with aliphatic diazo compounds and then decompose at low temperatures so slowly that catalysts must be added to accelerate the process. Suitable catalysts are strongly polar or surface-active substances whose field probably upsets the electronic equilibrium in the extremely unstable system of atoms of the polar diazo molecule. The latter breaks down into nitrogen and alkylene radicals. As catalyst we used copper bronze powder or anhydrous copper sulfate. Addition of catalyst accelerates the reaction 10-15 times.

The rate of hydrolysis of alkyl halides of silicon is known to fall in the order $RSiX_3$, R_2SiX_2, R_3SiX. This is probably bound up on the one hand with the reduced polarity of the Si-X bond and on the other hand with the growth of the screening effect of the alkyl groups. If this is so, then we can also account for the corresponding change in the effect of silicon alkyl halides on the decomposition of diazo compounds. This effect falls off in the above series of alkylhalosilanes, possibly for this reason.

With rise of reaction temperature to above –15° the rate of decomposition of the diazo compounds increases but the yields of organosilicon compounds sharply decrease since considerable amounts of "polymethylene" are formed due to the concurrent reaction of polymerization of the methylene radicals.

We therefore suggest that in the preparation of organosilicon compounds by the diazo method the free alkylene radical is formed but is attached to the Si-X bond and cannot polymerize. This hypothesis is consistent with the results of a study of the reaction of diazomethane with other silicon halides (fluorides and bromides).

Silicon tetrafluoride, which even in small amounts decomposes diazomethane, does not form organosilicon compounds with diazomethane. The Si-F bond energy is known to be very high (143 kcal). We may therefore assume that the activation energy of methylene polymerization is incomparably smaller than the reaction energy of methylenation of SiF_4, and consequently the reaction is exclusively directed towards polymethylene formation.

Reaction of diazomethane with silicon tetrabromide proceeds less energetically than that with the tetrachloride and at a lower velocity, but the ease of introduction of methylene groups increases since the Si-Br bond energy (69 kcal) is considerably lower than the Si-Cl bond energy (85.8 kcal). In this case the yields of organosilicon compounds increase and formation of di- and trialkylsilanes proceeds much more readily than with $SiCl_4$. Moreover, methylenation evidently continues to tetra-(brommethyl)-silane, but this compound could not be isolated in the pure state since it decomposes when distilled.

EXPERIMENTAL

a) Diazomethane and diazoethane were utilized in the form of 2.5-3% solutions in ether. These solutions were dried by freezing for 2-3 hours at −70° over solid KOH.

b) Silicon tetrachloride was distilled to remove hydrogen chloride.

c) Silicon tetrabromide. Dry bromine vapor was slowly passed at 500-520° through a tube filled with pellets of 70% Si-30% Fe alloy (ferrosilicon). The condensate — a light-colored, heavy, oily liquid — was fractionated. Traces of bromine were removed by shaking with mercury. Yield of substance with b.p. 151-153° was 65-75% calculated on the bromine used.

1. Preparation of chlormethyltrichlorsilane. To a solution of 85 g (1.5 mole) $SiCl_4$ in 100 ml dry ether at −45-55° was run in, with stirring, 13-14 g (1 mole) of diazomethane in 400 ml ether. The temperature in the reaction mixture must not be allowed to exceed the stated limits. The reaction is energetic and is accompanied by evolution of nitrogen (9 l. in all). After the color of diazomethane had disappeared and evolution of nitrogen had ceased, the temperature of the reaction mixture was slowly raised to room temperature and the ether and excess of $SiCl_4$ distilled off through a column. The residue was fractionated. Chlormethyltrichlorsilane has b.p. 116.5° at 750 mm; d_{20}^{20} 1.4776. Mobile colorless liquid with a pungent odor; hydrolyzes in the air.

4.440 mg, 4.930 mg substance: 1.020 mg, 1.185 mg CO_2. 0.495 mg, 0.695 mg H_2O. 0.4996 g substance: 0.1655 • g SiO_2. 12.850 mg, 11.920 mg substance: 13.85 ml, 12.85 ml 0.02 N $AgNO_3$. 0.0842 g, 0.3070 g substance: 13.35 ml, 50.05 ml 0.1 N $AgNO_3$. •• 0.3760 g substance; 15.48 g benzene: Δt 0.674°. Found %: C 6.27, 6.52; H 1.25, 1.09; Si • 15.44; total Cl 76.53, 76.53; hydrolyzable Cl. •• 57.32. 57.89; M 185. $ClCH_2SiCl_3$. Calculated %: C 6.52; H 1.09; Si 15.21; total Cl 77.11; hydrolyzable Cl 57.83; M 184.

The yield of chlormethyltrichlorsilane was 45-47% of theory (calculated on the diazomethane). The residue contained high-boiling chlormethylsilane chlorides (5-6 g) with b.p. 160-170°.

2. Preparation of di-(chlormethyl)-dichlorsilane $(ClCH_2)_2SiCl_2$. a) Using catalyst. To a mixture of 35 g (1 mole) chlormethyltrichlorsilane and 50 ml dry ether, cooled to −45-35°, is added 0.5 g finely pulverized anhydrous $CuSO_4$ and dropwise addition is made of half of a solution of 13.6 g (1.6 mole) diazomethane in 360 ml ether. The reaction is sluggish and is accompanied by evolution of nitrogen. After 3 hours the temperature in the reaction is raised to −20°, a further 0.5 g copper sulfate is added, and the second half of the diazomethane solution is added gradually (a portion being added when the color of the previous portion has disappeared). After about 8 l. nitrogen have come off, the reaction mixture is slowly brought to room temperature, the solution is filtered off from the separated polymethylene, and the ether distilled off in a column.

Several fractionations of the residue yielded di-(chlormethyl)-dichlorsilane with b.p. 58.5° at 16 mm; d_{20}^{20} 1.4624; 45% yield (based on diazomethane).

• Silicon was determined gravimetrically as SiO_2. The sample was burned with a 1:1 mixture of nitric and sulfuric acids.

•• Hydrolyzable chlorine was determined by titration of the aqueous hydrolyzate of the sample in ether.

4.670 mg substance: 2.095 mg CO_2; 0.965 mg H_2O. 0.5495 g substance: 0.1635 g SiO_2. 12.650 mg substance: 12.59 ml 0.02 N $AgNO_3$. 0.1277 g, 0.1608 g substance: 13.1 ml, 16.45 ml 0.1 N $AgNO_3$. 0.2376 g substance; 16.4 g benzene: Δt 0.370°. Found %: C 12.23; H 2.31; Si 13.85; total Cl 72.55; hydrolyzable Cl 36.13; M 200. $(ClCH_2)_2SiCl_2$. Calculated %: C 12.12; H 2.02; Si 14.14; total Cl 72.87; hydrolyzable Cl 35.86; M 198. The high boiling residue (80-90° at 15 mm) consisted of resinified products of further methylenation.

b) In absence of catalyst. A solution of 6.5 g diazomethane in 300 ml ether at −35-25° is gradually added to a mixture of 18.5 g $ClCH_2SiCl_3$ and 25 ml ether. After disappearance of the diazomethane color, the precipitate is filtered off and the ether distilled off in a column. Repeated fractionation gives di-(chlormethyl)-dichlorsilane with b.p. 57-59° at 16 mm in 30-35% yield (based on the diazomethane).

3. Preparation of tri-(chlormethyl)-chlorsilane $(ClCH_2)_3SiCl$. To 33 g (1 mole) di-(chlormethyl)-dichlorsilane in 50 ml ether is added 1 g anhydrous $CuSO_4$ and dropwise addition is made at −25-35° of 14.5 g (2 moles) of diazomethane in 400 ml ether; nitrogen is evolved and the original $(ClCH_2)_2SiCl_2$, which separates on cooling, goes into solution. The reaction is completed after 2 hours, the temperature of the mixture is then gradually brought to room temperature, the ethereal solution is filtered, and the ether distilled off in a column. Fractionation of the residue gives tri-(chlormethyl)-chlorsilane with b.p. 70° at 4 mm; d_{20}^{20} 1.4377. Yield 10-15% on the diazomethane.

3.380 mg, 4.680 mg substance: 2.100 mg, 2.920 mg CO_2; 1.065 mg, 1.350 mg H_2O. 15.380 mg, 9.490 mg substance: 14.17 ml, 8.75 ml 0.02 N $AgNO_3$. 0.1420 g, 0.1469 g substance: 6.90 ml, 7.10 ml 0.1 N $AgNO_3$. 0.3884 g substance; 16.0 g benzene: Δt 0.595. Found %: C 16.94, 17.01; H 3.52, 3.22; total Cl 65.30, 65.40; hydrolyzable Cl 17.25, 17.19; M 211. $(ClCH_2)_3SiCl$. Calculated %: C 16.98; H 2.83; total Cl 66.93; hydrolyzable Cl 16.72; M 212.

Residue in flask: A thick resin decomposing when heated.

4. Preparation of methyl-(chlormethyl)-dichlorsilane $CH_3Si(CH_2Cl)Cl_2$. a) Copper bronze as catalyst. 14.5 g (1.3 mole) diazomethane in 350 ml ether is added dropwise to 39 g (1 mole) methyltrichlorsilane in 40 ml ether. The reaction is started at −30° and then continues at −15°. The catalyst is 0.2 g powdered copper bronze. When the whole of the diazomethane had disappeared from solution (indicated by decolorization) the temperature was raised to room temperature; the solution was then filtered and the ether taken off through a column. Fractionation of the residue gave methyl-(chlormethyl)-dichlorsilane with b.p. 121-122°; d_{20}^{20} 1.2778. Yield 13% on the diazomethane. The substance was identical with that described by Krieble and Elliott [3]. Found % C 14.96, 14.80; H 3.20, 3.22; total Cl 70.85; hydrolyzable Cl 43.57, 43.76. $CH_3Si(CH_2Cl)Cl_2$. Calculated %: C 14.68; H 3.06; total Cl 71.34; hydrolyzable Cl 43.46.

b) Anhydrous $CuSO_4$ as catalyst. To 18 g CH_3SiCl_3 in 20 ml ether in presence of 0.5 g $CuSO_4$ is added dropwise at −30° 7.5 g diazomethane in 220 ml ether. Decomposition of the diazomethane is completed in one hour and the solution is then filtered, the ether taken off in a column and the residue fractionated. The 121-122° fraction of $CH_3Si(CH_2Cl)Cl_2$ is obtained in a yield of 12% of theory based on the diazo compound.

5. Reaction of diazomethane with triethylchlorsilane. To 15 g triethylchlorsilane in 25 ml ether in presence of 0.5 g $CuSO_4$ is added dropwise at −10-15° a solution of 12.5 diazomethane in 400 ml ether. After 3 hours the diazomethane has disappeared from the reaction mixture. The ether is then distilled off and the residue fractionated. 7 g of a fraction with b.p. 54° at 85 mm or 144° * (original chloride) was collected; also 5 g of a fraction with b.p. 104-110° at 10 mm, free from halogen. Repeated fractionation gave b.p. 101-102° at 9 mm (228° at 755 mm) which corresponds to the boiling point of triethylsilane oxide. Found %: C 57.70; H 11.98; M 238. $[(C_2H_5)_3Si]_2O$. Calculated %: C 58.54; H 12.14; M 246.

The same reaction was performed in the absence of catalyst in the course of a week at 0°; the same products were obtained.

6. Preparation of α-chlorethyltrichlorsilane $CH_3CHClSiCl_3$. To 84 g (2 moles) $SiCl_4$ in 100 ml ether is added dropwise, at −45-50° and with vigorous stirring, a solution of 14 g (1 mole) diazomethane in 450 ml ether. The reaction proceeds energetically with evolution of nitrogen (6.5 l.) and separation of a small amount of "polyalkylene". The reaction mixture is then brought to room temperature, the solution filtered and the

* Pressure not stated − Publisher.

ether taken off in a column. Repeated distillation of the residue gave α-chlorethylchlorsilane with b.p. 66° at 75 mm; d_{20}^{20} 1.3919. Yield 35% based on the diazo compound. Found %: Si 14.32; total Cl 70.52; hydrolyzed Cl 51.18; M 187. $CH_3CHClSiCl_3$. Calculated %: Si 14.15; total Cl 71.68; hydrolyzed Cl 53.76; M 198.

Residue: Resinous organosilicon products, a large proportion (5-6 g) distilled in the range of 80° at 75 mm to 175° at 50 mm.

7. Preparation of brommethyltribromsilane $BrCH_2SiBr_3$. To 52 g $SiBr_4$ in 60 ml ether is added, at −55-60° and with stirring, 5.5-6 g (1.1 mole) diazomethane in 200 ml ether. The reaction proceeds energetically with evolution of 4 l nitrogen. After distilling off the ether the residue was distilled twice to give 29 g (55% yield) of brommethyltribromsilane: b.p. 70° at 6 mm; d_{20}^{20} 2.5730.

5.950 mg substance: 0.820 mg CO_2; 0.380 mg H_2O. 0.7920 g substance: 0.1368 g SiO_2. 0.0885 mg substance: 7.30 ml 0.1 N $AgNO_3$. 13.590 mg substance: 7.397 ml 0.02 N $AgNO_3$. 0.3012 g substance: 16.0 benzene; Δt 0.270°. Found %: C 3.75; H 0.74; Si 8.06; Br total 86.98; Br hydrolyzed 65.86; M 357.0. $BrCH_2SiBr_3$. Calculated %: C 3.33; H 0.55; Si 7.75; Br total 88.41; Br hydrolyzed 66.29; M 36.17.

Residue: High-boiling brommethylated organosilicon compounds distilling at up to 110° at 10 mm.

8. Preparation of di-(brommethyl)-dibromsilane $(BrCH_2)_2SiBr_2$. To 62 g (1 mole) $SiBr_4$ in 80 ml ether is added at −50° and with intensive stirring 13 g (1.8 mole) diazomethane in 400 ml ether. The reaction is rapidly completed with evolution of about 8 5 l nitrogen. After distilling off the ether the residue is fractionated. Di-(brommethyl)-dibromsilane with b.p. 107° at 9 mm and d_{20}^{20} 2.4614 is obtained in 55% of the theoretical yield (on diazomethane).

6.765 mg substance: 1.730 mg CO_2; 0.970 mg H_2O. 0.7294 g substance: 0.1218 g SiO_2. 12.605 g substance: 6.040 ml 0.02 N $AgNO_3$. 0.1736 g substance: 9.20 ml 0.1 N $AgNO_3$. 0.1811 g substance; 16 g benzene: Δt 0.155°. Found %: C 6.98; H 1.60; Si 7.81; Br total 83.21; Br hydrolyzed 42.35; M 375. $(BrCH_2)_2SiBr_2$. Calculated %: C 6.38; H 1.06; Si 7.45; Br total 85.09; Br hydrolyzed 42.54; M 375.6.

The high-boiling fraction consisted of organosilicon products distilling up to 120° at 5 mm.

9. Preparation of tri-(brommethyl)-bromsilane $(BrCH_2)_3SiBr$. To 32 g (1 mole) $(BrCH_2)_2SiBr_2$ in 80 ml ether at −35-30° is added dropwise and with stirring 4.3 g (1.2 mole) diazomethane in 150 ml ether. Decomposition of the diazomethane is slow and is completed in 2-3 hours. The temperature is then raised to room temperature, the ether distilled off and the residue fractionated in vacuum, the last stage being accompanied finally by considerable decomposition. Tri-(brommethyl)-bromsilane with b.p. 122-123° at 5 mm and d_{20}^{20} 2.3440 is obtained in a yield of 40% (calculated on the diazomethane).

0.1642 g substance (2 hrs at 140° with 0.6 g Na in 5 ml alcohol): 16.75 ml 0.1 N $AgNO_3$. 0.3529 g substance (in ether, hydrolyzed with 25 ml water): 9.43 ml 0.1 N $AgNO_3$. 0.5740 g substance: 16 g benzene: Δt 0.485°. Found %: Br total 81.51; Br hydrolyzed 20.99; M 379. $(BrCH_2)_3SiBr$. Calculated %: Br total 82.02; Br hydrolyzed 20.50; M 389.6.

Residue: An organosilicon product decomposing when heated.

10. Preparation of tri-(brommethyl)-silane oxide $[(BrCH_2)_3Si]_2O$. 1 g of $(BrCH_2)_3SiBr$ on a watch glass is left overnight in the air. In the morning the mass crystallized. The crystals are pressed on porous tile and recrystallized from methanol. Needles with m.p. 69.5-70°. Quantitative yield.

4.700 mg substance: 2.000 mg CO_2; 0.760 mg H_2O. 0.9130 mg substance: 4.342 ml 0.02 N $AgNO_3$. 0.2035 g substance; 16 g benzene: Δt 0.120°. Found %: C 11.61; H 1.80; Br 75.99; M 618*. $[(BrCH_2)_3Si]_2O$. Calculated %: C 11.32; H 1.88; Br 75.54; M 635.5.

SUMMARY

1. It is found that the diazo method of synthesis of aliphatic organoelement compounds can be successfully extended to the preparation of organosilicon compounds.

* The cryoscopic constant for benzene is taken as 58.4 with allowance for the special characteristics of cryoscopic determination of molecular weights of the silane oxides (see [2]).

2. Silicon tetrachloride and silicon tetrabromide readily react with diazomethane and diazoethane to form primary, secondary and tertiary α-haloalkyl derivatives of silicon. Silicon tetrafluoride does not form organosilicon compounds by this reaction.

3. Alkylsilicon halides such as CH_3SiCl_3 and $(C_2H_5)_3SiCl$ enter with difficulty into reaction with aliphatic diazo compounds.

The reaction is facilitated by the use of powdered copper or copper salts, but even with their help triethylchlorsilane does not form compounds containing the α-haloalkyl radical.

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Received February 21, 1951

* See Consultants Bureau translation, p. 1569.
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SYNTHESIS OF ORGANOELEMENT COMPOUNDS OF THE ALIPHATIC SERIES BY THE DIAZO METHOD

IV. SYNTHESIS OF COMPOUNDS OF THE GROUP IV ELEMENTS — ORGANOTIN COMPOUNDS

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It has been previously shown that with the help of aliphatic diazo compounds organo-arsenic, -antimony, -bismuth, -phosphorous, and -silicon compounds can be synthesized [1]. This communication describes the results of a study of the diazo method of synthesis of organotin compounds.

Haloalkyl derivatives of tin have not previously been described in the literature, with the exception of di-(β-chlorovinyl)-tin, prepared by A. N. Nesmeyanov and co-workers [2]. Attempts to prepare α-haloalkyl derivatives of tin by the diazo method were unsuccessful [3].

We found that in a benzene medium at 0 to 5° diazomethane normally reacts with tin tetrachloride to form the whole range of possible chloromethylated derivatives of tin in a yield of 30-40% (calculated on the diazomethane). Alkylation of tin proceeds very easily, and even with a ratio of 1.5 mole $SnCl_4$ to 1 mole diazomethane there is formed, side by side with chloromethyltrichloro tin, di-(chloromethyl)-dichlorotin and tri-(chloromethyl)-chlorotin. The last compound has a boiling point close to that of dichloromethyltin and is separated from it with difficulty.

By treating chloromethyltrichlorotin or $SnCl_4$ with excess diazomethane (6 mole to 1 mole of chloride) it is possible to prepare tetrachloromethyltin in a yield of 50-60% (on the tin chloride). The following consecutive reactions may therefore be said to take place when diazomethane acts on $SnCl_4$:

$$SnCl_4 \xrightarrow[-N_2]{+CH_2N_2} ClCH_2SnCl_3 \xrightarrow[-N_2]{+CH_2N_2} (ClCH_2)_2SnCl_2 \xrightarrow[-N_2]{+CH_2N_2}$$

$$\longrightarrow (ClCH_2)_3SnCl \xrightarrow[-N_2]{+CH_2N_2} (ClCH_2)_4Sn.$$

Reaction of $SnBr_4$ with diazomethane proceeds in similar conditions even more readily and with high yields. With a 1:2 molar ratio the principal reaction products are: Di-(bromomethyl)-dibromotin and bromomethyltribromotin. Reaction of excess of diazomethane with di-(bromomethyl)-dibromotin (3:1) gives tetra-(bromomethyl)-tin.

Diazoethane acts on $SnCl_4$ in a similar manner to diazomethane. In this case, however, even with 2:1 molar ratio of $SnCl_4$ to diazoethane the main reaction product is di-(α-chloroethyl)-dichlorotin, together with tri-(α-chloroethyl)-chlorotin and α-chloroethyltrichlorotin (the latter is difficult to isolate in the pure form). Treatment of tri-(α-chloroethyl)-chlorotin with a large excess of diazoethane (1 mole of the tin compound to 3 moles of diazoethane) gives tetra (α-chloroethyl)-tin. Reaction of diazoethane with $SnCl_4$ may be represented by a scheme similar to that for diazomethane.

The main product of reaction of diazobutane with $SnCl_4$ in the molar ratio of 2:1 is di-(α-chlorobutyl)-dichlorotin:

$$2CH_3CH_2CH_2CHN_2 + SnCl_4 \longrightarrow (CH_3CH_2CH_2CHCl)_2SnCl_2 + 2N_2 .$$

The diazo method makes possible the synthesis of organotin compounds containing various α-haloalkyl radicals or compounds containing both unsubstituted and α-halo radicals. For example chloromethyl-di-(α-chloroethyl)-chlorotin can be obtained by reacting chloromethyltrichlorotin with diazoethane:

$$ClCH_2SnCl_3 + 2CH_3CHN_2 \longrightarrow ClCH_2SnCl(CHClCH_3)_2 + 2N_2.$$

Di-(chloromethyl)-dichlorotin and diazoethane give di-(chloromethyl)-di-(α-chloroethyl)-tin:

$(ClCH_2)_2SnCl_2 + 2CH_3CHN_2 \longrightarrow (ClCH_2)_2Sn(CHClCH_3)_2 + 2N_2$.

α-Chloroalkyl dichlorotin compounds enter readily into reaction with organomagnesium compounds to form mixed alkyl-α-chloroalkyl derivatives of tin. Thus, di-(α-chloroethyl)-dichlorotin with ethyl magnesium bromide gives di-(α-chloroethyl)-diethyltin:

$(CH_3CHCl)_2SnCl_2 + 2C_2H_5MgBr \longrightarrow (CH_3CHCl)_2Sn(C_2H_5)_2 + 2MgClBr$.

The above examples sufficiently clearly illustrate the general character of the reactions of tin halides containing tetravalent Sn with aliphatic diazo compounds. They represent a new synthesis of organotin compounds of the aliphatic series.

EXPERIMENTAL

1. Reaction of Diazomethane with Tin Tetrachloride

a) Preparation of chloromethyltrichlorotin and di-(chloromethyl)-dichlorotin side by side with trichloromethylchlorotin. To a solution of 34.5 ml (78.5 g or 0.3 mole) $SnCl_4$ in 50 ml dry benzene (thiophene-free), contained in a flask fitted with a mercury-sealed stirrer, a gas discharge tube, a thermometer and dropping funnel, is added over a period of 1-1½ hours at -5° a benzene solution of diazomethane (9 g or 0.2 mole in 500 ml benzene) which has previously been dried for 1-1½ hours over potassium hydroxide pellets.

The energetic reaction is accompanied by nitrogen evolution and by the formation of a precipitate which dissolves there and then. The mixture was then left overnight. The precipitate was filtered off and the benzene distilled off in a good column. The residual benzene and $SnCl_4$ were distilled off without a column. The resultant dark, mobile oil (26 g), which fumes in the air, was vacuum-distilled. Chloromethyltrichlorotin (10.5 g) comes over at 70-78° at 5 mm; this was followed at 110-125° (5 mm) by a mixture of di-(chloromethyl)-dichlorotin and tri-(chloromethyl)-chlorotin (5.5 g). During the fractionation the dichloride begins to crystallize in the form of white needles. The residue was a solid dark resin (2 g).

Repeated fractionation of the 70-78° fraction at 5 mm yielded pure chloromethyltrichlorotin in the form of a heavy, colorless, oily liquid, fuming slightly in the air and gradually darkening in storage. B.p. 72.5-73° at 5 mm; d_2^{20} 2.1; n_D^{20} 1.5318. It mixes with the common solvents, dissolves in water and hydrolyzes.

0.2400 g, 0.2320 g substance: 25.9 ml, 25.02 ml 0.1 N $AgNO_3$. 10.365 mg, 11.780 mg substance: 7.36 ml, 8.49 ml 0.02 N $AgNO_3$. 5.920 mg, 5.670 mg substance: 1.085 mg, 1.005 mg CO_2; 0.850 mg, 0.735 mg H_2O. 0.4625 g, 0.8137 g substance: 21.32 benzene: Δt 0.405°, 0.720°. 0.4112 g substance: 0.2256 g SnO_2. Found %: C 5.00, 5.12; H 1.6, 1.45; Cl hydrolyzed 38.27, 38.24; total Cl 50.41, 51.65; Sn 43.12; M 274.5, 271.7. $ClCH_2SnCl_3$. Calculated %: C 4.37; H 0.73; Cl hydrolyzed 38.76; Cl total 51.66; Sn 43.23; M 274.5.

Di-(chloromethyl)-dichlorotin can be separated from its mixture with tri-(chloromethyl)-tin by removing the oil on a porous porcelain plate or by dissolving the mixture in boiling benzene, the dichloride then crystallizing out in the pure form.

Di-(chloromethyl)-dichlorotin crystallizes well from cyclohexane in the form of white rectangular prisms or from gasoline in the form of large, lustrous, white needles; it is readily soluble under normal conditions in benzene, alcohol and water. M.p. 89.5-90° (falling to 83°).

6.230 mg, 8.005 mg substance: 3.300 mg, 4.212 mg SnO_2. 6.615 mg, 8.305 mg substance: 2.060 mg, 2.570 mg CO_2; 1.070 mg, 1.135 mg H_2O. 0.1418 g, 0.1400 g substance: 9.83 ml, 9.73 ml 0.1 N $AgNO_3$.* 15.920 mg, 13.225 mg substance: 10.85 ml, 9.08 ml 0.02 N $AgNO_3$. 0.2516 g, 0.3416 g substance: 17.11 g benzene: Δt 0.25°, 0.34°. Found %: Sn 41.72, 41.75; C 8.51, 8.44; H 1.80, 1.53; Cl hydrolyzed 24.57, 24.65; total Cl 48.35, 48.70; M 301.1, 300.7. $(ClCH_2)_2SnCl_2$. Calculated %: Sn 41.13; C 8.51; H 1.39; Cl hydrolyzed 24.58; total Cl 49.22; M 288.58.

* Hydrolyzable chlorine was determined by dissolving a weighed sample in water, then adding excess of 0.1 N $AgNO_3$ and back-titrating. Preliminary treatment of the solution of dichloride with caustic alkali would lead to too-high and variable results probably due to hydrolysis of the chlorine linked to carbon atoms.

Tri-(chloromethyl)-chlorotin in the slightly impure form could be isolated by fractionation of the above-described mixture obtained from three operations. Several fractionations (the dichloride comes off first) leaves an uncrystallizable oil – tri-(chloromethyl)-chlorotin; b.p. 138-140° at 5 mm; d_{20}^{20} 2.03; n_D^{20} 1.593.

The compound is soluble in common solvents and in water. Alkalization of the aqueous solution yields a precipitate soluble in excess alkali.

Found %: Cl hydrolyzed 11.66, 11.89; Cl total 43.65, 43.51. $(CH_2Cl)_3SnCl$. Calculated %: Cl hydrolyzed 11.74; Cl total 45.38.

30 g diazomethane gave 62 g of a mixture of chloromethyl derivatives (about 30% of the theoretical yield).

b) Preparation of tetra-(chloromethyl)-tin. preparation from chloromethyltrichlorotin and diazomethane. To a solution of 9 g chloromethyltrichlorotin in 25 ml benzene is gradually added, with stirring, a benzene solution of diazomethane (7.8 g in 270 ml or 1:6 molar ratio) at 3-6°. The mixture is left overnight. The excess of diazomethane is decomposed with anhydrous copper sulfate by gradual addition of the reaction solution with stirring to a suspension of 1 g $CuSO_4$ in 25 ml benzene. The residue is filtered off and the benzene distilled off in a column.

The residue of dark oil crystallized on cooling (8.5 g) and was distilled in vacuum when a colorless, rapidly crystallizing oil came over; this was tetra-(chloromethyl)-tin (5.5 g) with b.p. 147-150° at 8 mm. Yield 52% of the theoretical based on the chloromethyltrichlorotin.

Tetra-(chloromethyl)-tin is readily soluble in benzene and alcohol and insoluble in water. It crystallizes from gasoline (1:10) as well-formed lustrous, white needles. M.p. 49-49.5° (begins to fuse at 48°). B.p. 148.5° at 8 mm.

15.315 mg, 9.395 mg substance: 9.455 ml, 5.753 ml 0.02 N $AgNO_3$. 8.645 mg, 5.955 mg substance: 4.830 mg, 3.250 mg CO_2; 2.230 mg, 1.425 mg H_2O. 15.230 mg, 9.135 mg substance: 7.222 mg, 4.36 mg SnO_2. Found %: Sn 37.36, 36.60; C 15.23, 14.88; H 2.88, 2.68; Cl 43.80, 43.43 $(CH_2Cl)_4Sn$. Calculated %: Sn 37.49; C 15.16; H 2.53; Cl 44.8.

Preparation from tin tetrachloride and diazomethane. To a solution of 34.7 g (1 mole) $SnCl_4$ in 50 ml dry benzene was added, as described above, a solution of 33.4 g (6 mole) diazomethane in 850 ml benzene at 3-6°. The reaction mixture is left overnight. The excess of diazomethane was decomposed as above. The benzene was distilled off with the help of a dephlegmator and the residue fractionated in vacuum. Tetra-(chloromethyl)-tin came over at 170-174° (20 mm) as a rapidly crystallizing oil (24 g). The resin remaining in the flask decomposed when heated. M.p. of tetra-(chloromethyl)-tin is 48-49°. No depression of m.p. of a mixed sample with the tetra-(chloromethyl)-tin prepared as described above. Yield 57% of theory based on tin tetrachloride.

2. Reaction of Diazomethane with Tin Tetrabromide

a) Preparation of bromomethyltribromotin together with di-(bromomethyl)-dibromotin. To a solution of 91 g $SnBr_4$ (0.2 mole) in 60 ml benzene is added a dry benzene solution of diazomethane (17.5 g or 0.4 mole in 400 ml). The benzene solution was previously dried over potassium hydroxide pellets for 2 hrs. The diazomethane solution is added at 1-2°. The reaction proceeds energetically with vigorous evolution of nitrogen. The mixture is left overnight, filtered from the small precipitate, and distilled in vacuum to remove the benzene. The residual mixture (about 78 g) is distilled at 5 mm to give the following fractions: I) b.p. 70-135° (21.5 g); II) b.p. 155-160° (44.0 g); III) b.p. 165-180° (about 0.5 g); the residue of hard resin weighed 12.5 g.

After a second fractionation of the 70-135° fraction, pure bromomethyltribromotin (5 g) is isolated with b.p. 109° at 5 mm; it is a heavy colorless liquid with d_{20}^{20} 3.251; miscible with water and soluble in common organic solvents.

3.488 mg substance: 0.375 mg CO_2; 0.414 mg H_2O. 4.697 mg substance: 0.488 mg CO_2; 0.482 mg H_2O. 0.3308 g substance: 21.53 ml 0.1 N $AgNO_3$. 0.3936 g substance: 26.18 ml 0.1 N $AgNO_3$. 17.440 mg substance: 7.75 ml 0.02 N $AgNO_3$. 11.940 mg substance: 5.34 ml 0.02 N $AgNO_3$ 8.518 mg substance: 2.883 mg SnO_2. 7.705 mg substance: 2.585 mg SnO_2. Found %: C 2.93, 2.82; H 1.32, 1.15; Br hydrolyzed 52.0, 52.15; Br total 71.16, 71.50; Sn 26.66, 26.42; $BrCH_2SnBr_3$. Calculated %: C 2.65; H 0.43; Br hydrolyzed 53.0; Br total 70.3, Sn 26.23.

The colorless, rapidly crystallizing di-(bromomethyl)-dibromotin (44 g) comes over at 155-160°; it crystallizes from benzene as large, white rectangular prisms with m.p. 87°; readily soluble in water and common solvents.

4.492 mg substance: 0.905 mg CO_2; 0.618 mg H_2O. 4.926 mg substance: 1.022 mg CO_2; 0.630 mg H_2O 18.670 mg substance: 8.19 ml 0.02 N $AgNO_3$. 14.230 mg substance : 6.39 ml 0.02 N $AgNO_3$. 0.4320 g substance: 18.24 ml 0.1 N $AgNO_3$. 0.1322 g substance: 5.62 ml 0.1 N $AgNO_3$. 5.395 mg substance: 1.714 mg SnO_2. 4.720 mg substance: 1.490 mg SnO_2. Found %: C 5.49, 5.65; H 1.43, 1.50; Br hydrolyzed 33.8, 33.9; Br total 71.80, 71.82, Sn 25.02, 24.87. $(BrCH_2)_2SnBr_2$. Calculated % C 5.18; H 0.87; Br hydrolyzed 34.0; Br total 68.7 ; Sn 25.4.

Some material came over at 165-180°, but severe decomposition then started. A second fractionation of the 165-180° fraction gave a substance boiling at 165°, containing 18.8% hydrolyzable bromine and composed evidently of impure tri-(bromomethyl)-bromotin.

b) Preparation of tetra-(bromomethyl)-tin from di-(bromomethyl)-dibromotin and diazomethane. To a solution of 40 g di-(bromomethyl)-dibromotin in 50 ml dry benzene is added with stirring a solution of 12.8 g diazomethane in 500 ml benzene (molar ratio 1:3) at 3-2°. The reaction mixture was left overnight. The diazomethane excess was decomposed as before. The solution is filtered from precipitate, the benzene is distilled off on a water bath at 30-40° in vacuum. White crystals of tetra-(bromomethyl)-tin in the flask are impregnated with resin. The latter is washed out with benzene and the residual tetra-(bromomethyl)-tin crystallizes nicely from gasoline in the form of lustrous white needles with m.p. 57° (yield 25 g). Readily soluble in the common solvents and insoluble in water.

6.230 mg substance: 2.410 mg CO_2; 0.850 mg H_2O. 4.580 mg substance: 1.725 mg CO_2; 0.775 mg H_2O. 10.55 mg substance: 4.83 ml 0.02 N $AgNO_3$. 6.140 mg substance: 1.818 mg SnO_2. 4.989 mg substance: 1.506 mg SnO_2. Found %: C 10.54, 10.28; H 1.52, 1.89; Br 65.61; Sn 23.78, 23.33 $(BrCH_2)_4Sn$. Calculated %: C 9.82; H 1.64; Br 65.5; Sn 24.2.

3. Reaction of Diazoethane with Tin Tetrachloride

a) Preparation of di-(α-chloroethyl)-dichlorotin and tri-(α-chloroethyl)-chlorotin. To a solution of 220 g $SnCl_4$ (0.85 mole) in 150 ml dry benzene is slowly added from a dropping funnel a dry benzene solution of diazoethane (24 g or 0.43 mole in 800 ml benzene). The diazoethane solution was previously dried for 2 hours over potassium hydroxide pellets. Addition of diazoethane is effected over a period of 2.5 hours at 2-4°. The mixture is left overnight, then filtered from the small precipitate, and the benzene distilled off in a column. The residues of benzene and $SnCl_4$ are distilled off without a column; the vapor temperature rises to 116°. The resultant highly mobile liquid (70 g), fuming strongly in the air, is fractionated at 4 mm to give the following fractions: I) B.p. up to 60°, 11.3 g (contains $SnCl_4$); II) b.p. 60-104°, 18.1 g; III) b.p. 105-116°, 27.8 g; IV) b.p. 125-136°; residue 5.5 g.

A second fractionation of fraction II gave a substance with b.p. 69-71°. Judging by the analysis this is α-chloroethyltrichlorotin contaminated with di-(α-chloroethyl)-dichlorotin. Isolation of pure chloroethyl-trichlorotin was made difficult by the small amount of material.

13.52 mg substance: 8.831 ml 0.02 N $AgNO_3$. 13.01 mg substance: 8.47 ml 0.02 N $AgNO_3$. 3.688 mg, 3.498 mg substance: 1.380 mg, 1.318 mg CO_2; 1.007 mg, 0.883 mg H_2O. 11.49 mg, 11.760 mg substance: 5.675 mg, 5.730 mg SnO_2. 0.1443 g substance: 14.19 ml 0.1 N $AgNO_3$. Found %: C 10.20, 10.27; H 3.05, 2.82; Cl total 46.33, 46.17; Cl hydrolyzed 34.87; Sn 38.90, 38.42. $(CH_3CHCl)SnCl_3$. Calculated %: C 8.30; H 1.37; Cl 49.0; Cl hydrolyzed 36.9; Sn 41.4.

A second fractionation of the third fraction at 4 mm gave 10.5 g di-(α-chloroethyl)-dichlorotin with b.p. 112° at 4 mm: A colorless oily liquid, darkening on standing in the air; d_{20}^{20} 1.829; n_D^{20} 1.5535; crystallizes in white crystals with m.p. 12°.

0.0902 g, 0.0874 g substance: 5.6 ml, 5.45 ml 0.1 N $AgNO_3$. 8.91 mg, 14.49 mg substance: 5.58 ml 9.052 ml 0.02 N $AgNO_3$. 5.715 mg, 5.080 mg substance: 3.30 mg, 2.875 mg CO_2; 4.420 mg, 1.37 mg H_2O. 0.3645 g substance: 0.1758 g SnO_2. 0.1771 g, 0.1252 g substance; 20 g benzene: Δt 0.140°, 0.10°. Found %: C 15.43, 15.39; H 2.78, 3.01; Cl total 44.41, 44.30; Cl hydrolyzed 22.10, 22.08; Sn 37.75; M 320.5, 323.8 $(CH_3CHCl)_2SnCl_2$. Calculated %: C 15.16; H 2.54; Cl total 44.8; Cl hydrolyzed 22.42; Sn 37.48; M 316.7.

A second fractionation of fraction IV gave tri-(chloroethyl)-chlorotin (7.5 g) with b.p. 130° at 3 mm; a colorless oily liquid, easily soluble in the common solvents; d_{20}^{20} 1.684; n_D^{20} 1.5450.

5.100 mg substance: 3.895 mg CO_2; 1.640 mg H_2O. 18.015 mg, 15.38 mg substance: 10.16 ml, 8.731 ml 0.02 N $AgNO_3$. 0.1550 g substance: 4.94 ml 0.1 N $AgNO_3$. 7.226 mg, 7.650 mg substance: 3.12 mg, 3.335 mg SnO_2. 0.1520 mg substance; 20 g benzene: Δt 0.115°. Found %: C 20.89; H 3.59; Cl total 40.00, 40.26; Cl hydrolyzed 11.3; Sn 34.01, 34.34; M 338.0 $(CH_3CHCl)_3SnCl$. Calculated %: C 20.88; H 3.48; Cl total 41.16; Cl hydrolyzed 10.3; Sn 34.43; M 344.6.

b) Preparation of tetra-(chloroethyl)-tin. To 26 g tri-(chloroethyl)-chlorotin, containing a small amount of di-(chloroethyl)-dichlorotin, in 50 ml dry benzene is gradually added 13.5 g diazoethane in 500 ml benzene at 2-3° (molar ratio of 1:3). Nitrogen is evolved energetically at first; after addition of 4 g diazoethane the evolution of nitrogen ceases. The temperature of the reaction mixture is brought to room temperature and the diazoethane is added at 15°. The mixture is left overnight, filtered from the small precipitate, and the benzene distilled off at 30-35° in vacuum. The remaining liquid (about 24 g), dark in color, is distilled in vacuum. The main portion (15.7 g) came over at 140-145° (3 mm); the residue (6.5 g) is a brown hard resin. A second distillation of the fraction yielded tetra-(chloroethyl)-tin (9.3 g) with b.p. 142° at 2 mm; very mobile, slightly colored liquid, readily soluble in common solvents; d_{20}^{20} 1.568; n_D^{20} 1.5365.

5.800 mg, 3.640 mg substance: 5.475 mg, 3.460 mg CO_2; 1.935 mg, 1.275 mg H_2O. 6.295 mg, 6.595 mg substance: 2.59 mg, 2.695 mg SnO_2. 10.025 mg substance: 5.98 ml 0.02 N $AgNO_3$ 15.010 mg substance: 7.774 ml 0.02 N $AgNO_3$. 0.2672 g, 0.6394 g substance; 20 g benzene: Δt 0.190, 0.450°. Found %: C 25.75, 26.91; H 3.73, 3.91; Cl 36.73, 37.37; Sn 32.41, 32.19; M 362.0, 363.7. $(CH_3CHCl)_4Sn$. Calculated %: C 26.0; H 4.30; Cl 38.2; Sn 31.8; M 372.5.

c) Preparation of di-(α-chloroethyl)-tin oxide. To a solution of 1 g di-(α-chloroethyl)-dichlorotin in 7 ml ethyl alcohol with stirring is added, dropwise, aqueous ammonia until the reaction is weakly alkaline. After 30 minutes the mixture is heated to boiling, the precipitate removed at the pump, washed with a little alcohol, and dried at 60-70°. Di-(α-chloroethyl)-tin oxide is a finely crystalline white powder with m.p. 180°. Yield 0.6 g.

Found %: C 18.70, 18.87; H 3.52, 3.85; Cl 27.48, 28.78; Sn 45.14, 45.35 $(CH_3CHCl)_2SnO$. Calculated %: C 18.34; H 3.08; Cl 27.10; Sn 45.30.

4. Reaction of Diazobutane with Tin Tetrachloride

Preparation of di-(α-chlorobutyl)-dichlorotin. To a solution of 46.5 g $SnCl_4$ in 50 ml dry benzene is added 7.5 g diazobutane in 480 ml benzene (molar ratio of 2:1) at 1°. The mixture is left overnight, filtered from a small precipitate, and the benzene taken off in vacuum at 30°. The residue (about 19.5 g) is fractionated in vacuum at 5 mm when the following fractions were obtained: I) b.p. 70-110°, 5.7 g; II) b.p. 110-145°, 8.3 g; residue of 5.4 g of dark, solid resin. A second distillation of fraction II gave 5.0 g with b.p. 134° at 5 mm which crystallized in the condenser and consisted, judging by the analysis, of di-(chlorobutyl)-dichlorotin; white crystals with m.p. 53°, readily soluble in common solvents.

4.635 mg substance: 4.480 mg CO_2; 1.760 mg H_2O. 3.960 mg substance: 3.825 mg CO_2; 1.515 mg H_2O. 10.42 mg substance: 5.521 ml 0.02 N $AgNO_3$. 13.70 mg substance: 7.327 ml 0.02 N $AgNO_3$. 0.1486 g substance: 0.0624 g SnO_2. Found %: C 26.35, 26.35; H 4.25, 4.18; Cl total 37.58, 37.93; Sn 32.6 $(CH_3CH_2CH_2CHCl)_2SnCl_2$. Calculated %: C 25.8; H 4.28; Cl total 38.00; Sn 31.83.

5. Preparation of Derivatives of Tetravalent Tin with Mixed Radicals

a) Preparation of chloromethyl-di-(α-chloroethyl)-chlorotin. To a solution of 20 g chloromethyltrichlorotin in 50 ml dry benzene is added a benzene solution of diazoethane (8.1 g in 400 ml, molar ratio 1:2) at 2-3°. The mixture is left overnight, then filtered from the small oily deposit, and the benzene taken off at 30-35° in vacuum. The residue (about 30 g), a dark, oily liquid, is distilled in vacuum.

Between 110 and 125° (at 3 mm) 2.8 g material comes over. The main bulk of product (22.75 g) distilled at 126-128° (3 mm). The residue is a dark, viscous resin (4.8 g). A second distillation of the 126-128° fraction gives pure chloromethyl-di-(α-chloroethyl)-chlorotin with b.p. 128° at 3 mm; d_{20}^{20} 1.765; n_D^{20} 1.555; a colorless oily liquid soluble in organic solvents. Yield 10.5 g.

7.195 mg, 5.015 mg substance: 4.700 mg, 3.235 mg CO_2; 2.160 mg, 1.535 mg H_2O. 13.030 mg substance: 7.654 ml 0.02 N $AgNO_3$. 13.210 mg substance: 7.852 ml 0.02 N $AgNO_3$. 10.385 mg, 8.952 mg substance: 4.785 mg, 4.093 mg SnO_2. 0.2275 g, 0.3352 g substance: 20 g benzene: Δt 0.190, 0.270°. Found %: C 17.81, 17.59; H 3.36, 3.42; Cl 41.66, 42.13; Sn 36.31, 36.01; M 320 315 $(CH_2CHCl)_2SnClCH_2Cl$. Calculated %: C 18.4; H 3.30; Cl 42.94; Sn 35.90; M 330.

b) Preparation of di-(chloromethyl)-di-(α-chloroethyl)-tin. To a solution of 10 g di-(chloromethyl)-[illegible] (1 mole) in 50 ml dry benzene is added a solution of 8.5 g diazoethane (4 moles) in 300 ml benzene at 2-4°. Nitrogen evolution ceases after about 3 g diazoethane has been added. The temperature is then raised to room temperature and the diazoethane is added at 10-12°. The mixture is left overnight, filtered from the precipitate, the benzene is distilled off in vacuum at 30-35° and the residue fractionated. [illegible] g comes over at 141-145° (5 mm). The residue (5 g) decomposes with further heating. After repeated distillation, the 141-145° fraction yields di-(chloromethyl)-di-(chloroethyl)-tin with b.p. 141-142° at 5 mm; oily colorless liquid, soluble in organic solvents; d_{20}^{20} 1.675; n_D^{20} 1.578.

Found %: C 21.81, 21.52; H 3.59, 3.54; Cl 40.63, 39.07; Sn 34.82, 33.68; M 338. $(CH_3CHCl)_2Sn(CH_2Cl)_2$. Calculated %: C 20.88; H 3.48; Cl 41.13; Sn 34.43; M 344.7.

c) Preparation of di-(α-chloroethyl)-diethyltin. To cooled Grignard reagent (3 g Mg, 13.5 g ethyl bromide and 47.5 ml absolute ether) with constant stirring and cooling is rapidly added 10 g di-(α-chloroethyl)-dichloro[illegible]. The mixture is refluxed for 3 hours on the water bath, part of the ether is driven off and the residue decomposed with water, then with saturated ammonium chloride solution and finally with hydrochloric acid. To the resulting mixture is added ether and the layers separated. The aqueous layer is subjected to two further extractions with a little ether, and the ethereal solution is dried over calcined sodium sulfate. The ether is driven off and the residue (about 7 g) is fractionated in vacuum. The main amount (3.5 g) comes over at 114-155° (6 mm); the residue of 0.8 g is a viscous oil which decomposes when heated. A second distillation gives a product at 114-115° (5 mm). Pure di-(α-chloroethyl)-diethyltin is a readily mobile, colorless liquid; d_{20}^{20} 1.414; n_D^{20} 1.5085; soluble in organic solvents. Found %: C 30.62, 30.97; H 6.56 6.33; Cl 22.85, 22.88; Sn 38.25, 38.13; M 303. $(CH_3CHCl)_2Sn(C_2H_5)_2$. Calculated %: C 31.16; H 5.92; Cl 23.45; Sn 39.2; M 303.7.

SUMMARY

1. It is shown that the diazo method of synthesis of aliphatic organoelement compounds can be successfully extended to organotin compounds.

2. A new diazo synthesis is developed for α-haloalkyl derivatives of tin by reaction of halogenated derivatives of tetravalent tin with aliphatic diazo compounds.

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Received February 21, 1951

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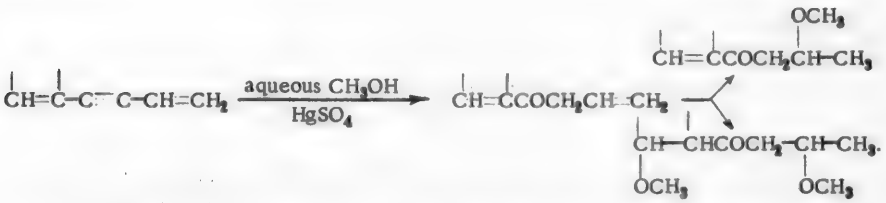
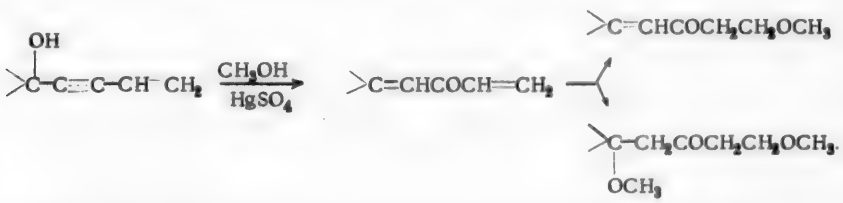
147. SYNTHESIS OF β-AMINO KETONES BY THE ACTION OF SECONDARY AMINES ON β-METHOXY KETONES

I. N. Nazarov and S. A. Vartanyan

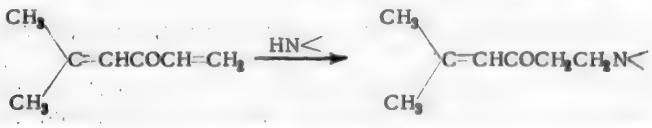
It has been shown in our laboratory that in the hydration of divinylacetylenic hydrocarbons in aqueous methanol in presence of mercuric sulfate, vinylallyl ketones are readily obtained which in the experimental conditions add on one or two molecules of methanol and are converted into the corresponding β-methoxy ketones [1]:



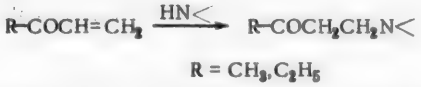
In another investigation in our laboratory it was shown that in presence of mercuric sulfate in methanol solution, vinylethinyl carbinols readily isomerize to divinyl ketones which in the experimental conditions add on methanol and are likewise converted into the corresponding β-methoxy ketones [2]:



β,β-Dimethyldivinyl ketone readily adds on secondary amines (diethylamine, piperidine) at the unsubstituted vinyl group with formation of unsaturated ketoamines [3]:

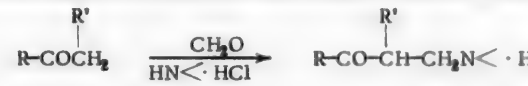


Similarly secondary amines add on to alkylvinyl ketones to form alkyl-β-aminoethyl ketones [4]:



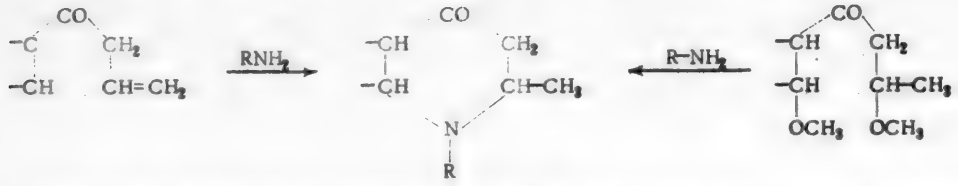
R = CH_3, C_2H_5

β-Amino ketones can also be obtained by the Mannich reaction [5] – action of secondary amine hydrochlorides in aqueous formaldehyde solution on saturated ketones:



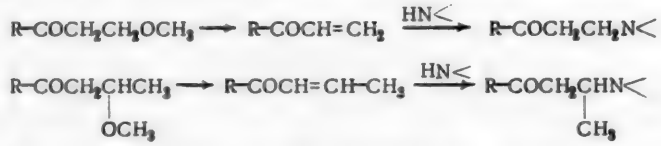
β-Amino ketones have recently been widely applied in the synthesis of diverse physiologically active substances [6], and therefore the development of simple methods of preparation of β-amino ketones may have great significance for the further progress of work on the discovery and synthesis of new pharmaceutical chemical preparations and medicinal products. For the preparation of β-amino ketones we decided first of all to utilize

the above-mentioned readily accessible β-methoxy ketones, on the basis of which had already been developed in our laboratory a new and simple method of preparation of diverse γ-piperidones [7]:



It was found that β-methoxy ketones readily react also with secondary amines to form the corresponding β-amino ketones in high yields, which are also obtained by direct addition of amines to α,β-unsaturated ketones.

The reaction of amines with β-methoxy ketones is facilitated in presence of water and it proceeds in all probability via the cleavage of methanol from the β-methoxy ketones followed by addition of the amine at the double bond of the unsaturated ketone:

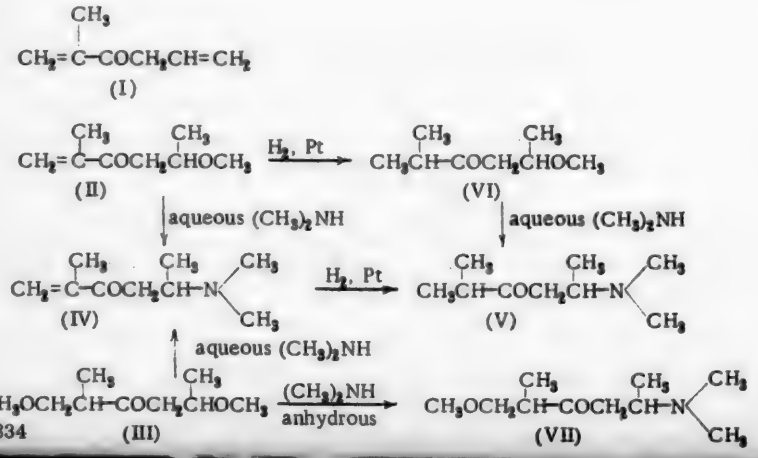


Experimental evidence has been obtained of the cleavage of methanol from β-methoxy ketones under the influence of amines in our experimental conditions. At the same time methoxy derivatives not containing a carbonyl group in the β-position and not susceptible to easy cleavage of methanol do not enter into reaction with ammonia and amines. Thus, for example, all our attempts to realize the reaction:

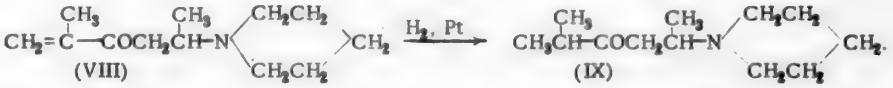
remained unsuccessful; the methoxy groups did not enter into reaction with ammonia even when heated (4 hours at 80°), and the dimethoxy carbinol was almost entirely recovered unchanged [8].

By reacting an aqueous solution of dimethylamine with allylisopropenyl ketone (I), 2-methyl-5-methoxy-1-hexen-3-one (II) and 1,5-dimethoxy-2-methylhexan-3-one (III) [1], a 60% yield of one and the same substance is obtained – 2-methyl-5-dimethylamino-1-hexen-3-one (IV); hydrogenation of the latter in alcohol solution in presence of Pt-catalyst results in absorption of one molecule of hydrogen to form 2-methyl-5-dimethyl-aminohexan-3-one (V).

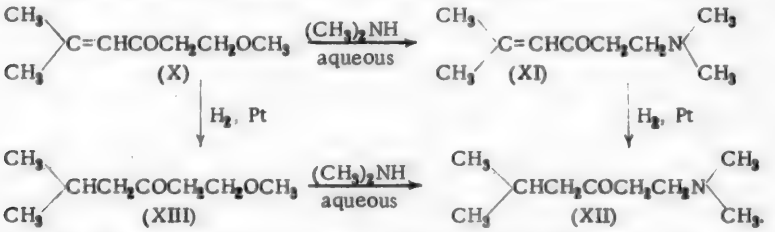
This ketone is also obtained by acting with aqueous dimethylamine on 2-methyl-5-methoxyhexan-3-one (VI) [1]:



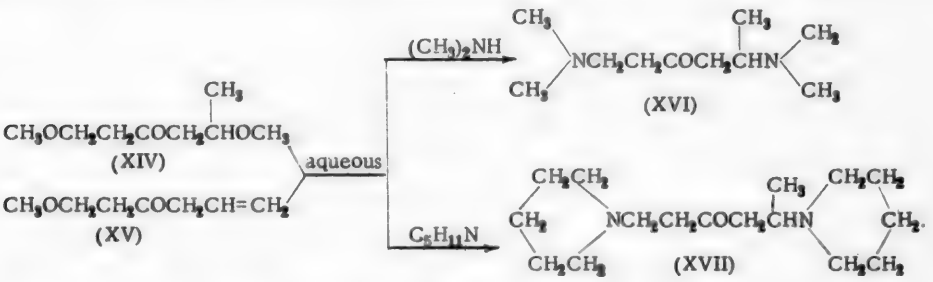
However, reaction of gaseous dimethylamine with the dimethoxy ketone (II) in an anhydrous medium gives 1-methoxy-2-methyl-5-dimethylaminohexan-3-one (VII) with retention of the methoxy group. These results show that water in the reaction mixture facilitates the cleavage of methanol from β-methoxy ketones, and this fact also explains its accelerating effect on this reaction. Reaction of aqueous piperidine solution with ketones (I, II, III) also gives one and the same substance in the shape of 2-methyl-5-N-piperidyl-1-hexen-3-one (VIII), hydrogenation of which in alcoholic solution in presence of Pt-catalyst leads to absorption of one molecule of hydrogen to form 2-methyl-5-N-piperidylhexan-3-one (IX):



Treatment of 2-methyl-6-methoxy-2-hexen-4-one (X) with aqueous dimethylamine [2] gives 2-methyl-6-dimethylamino-2-hexen-4-one (XI), hydrogenation of which in alcohol in presence of Pt absorbs one molecule of hydrogen to form 2-methyl-6-dimethyl-amino-hexan-4-one (XII). This amino ketone is also obtained by the action of dimethylamine on 2-methyl-6-methoxyhexan-3-one (XIII) [2,8]:

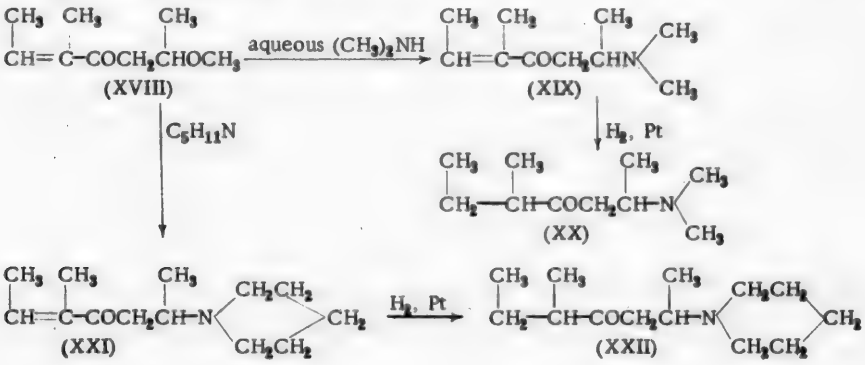


Reaction of dimethylamine with 1,5-dimethoxyhexan-3-one (XIV) and with 1-methoxy-5-hexen-3-one (XV) [9] gives a good yield of 1,5-bis-dimethylaminohexan-3-one (XVI):



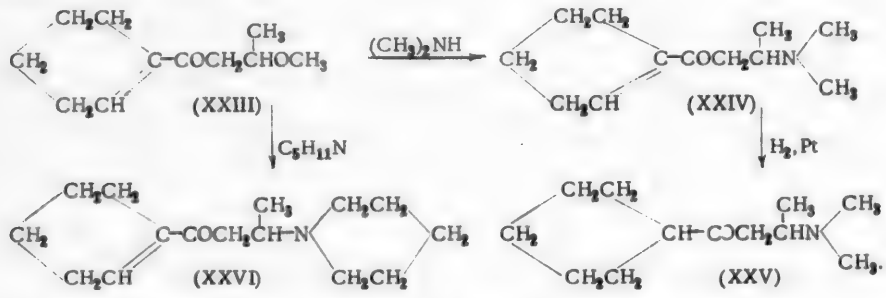
Reaction of aqueous solution of piperidine with ketones (XIV) and (XV) gives 1,5-bis-(N-piperidyl)-hexan-3-one (XVII) in good yield.

An aqueous solution of dimethylamine acts on 3-methyl-6-methoxy-2-hepten-4-one (XVIII) [10] to give, in a yield of about 55%, 3-methyl-6-dimethylamino-2-hepten-4-one (XIX). On hydrogenation in alcoholic solution in presence of Pt-catalyst, this amino ketone absorbs one molecule of hydrogen to form 3-methyl-6-dimethylamino-heptan-4-one (XX):



Piperidine acts on the methoxy ketone (XVIII) to form 3-methyl-6-(N-piperidyl)-2-heptan-4-one (XXI). This amino ketone hydrogenates in alcoholic solution in presence of Pt-catalyst to give 3-methyl-6-(N-piperidyl)-heptan-4-one (XXII).

Aqueous dimethylamine acts on allylcyclohexenyl ketone, also on its corresponding methoxy ketone (XXIII) [11], to give β-dimethylaminopropylcyclohexenyl ketone (XXIV). On hydrogenation in alcohol in presence of Pt-catalyst this amino ketone absorbs one molecule of hydrogen to form cyclohexyl-β-dimethylaminopropyl ketone (XXV):



An aqueous solution of piperidine reacts with the methoxy ketone (XXIII) to yield β-N-piperidylpropylcyclohexenyl ketone (XXVI).

All the β- amino ketones described in this paper are colorless liquids which turn yellow on standing and have a characteristic amine odor.

EXPERIMENTAL

Preparation of 2-methyl-5-dimethylamino-1-hexen-3-one (IV). a) 100 g 2-methyl-5-methoxy-1-hexen-3-one (II) (b.p. 54-59° at 6 mm; n_D^{20} 1.4400) [1] and 240 g 33 % aqueous dimethylamine solution were heated in an autoclave at 80° for 7 hours. The excess dimethylamine was removed in vacuum on a water bath at 45°. The solution was acidified with hydrochloric acid and the neutral products extracted with ether. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate and distilled in vacuum. There was obtained 72 g 2-methyl-5-dimethylamino-1-hexen-3-one (IV) as a liquid which turned yellow on standing and had a characteristic amine odor. B.p. 78-80° at 6 mm.

n_D^{20} 1.4560; d_4^{20} 0.8909; MR_D 47.30; calculated 47.24.

4.200 mg substance: 0.330 ml N_2 (20°, 740 mm). 2.444 mg substance: 0.195 ml N_2 (20°, 740 mm). Found %: N 8.91, 9.05. $C_9H_{17}ON$. Calculated %: N 9.03.

The picrate formed flat needles with m.p. 119-120° (from alcohol). From the neutral products was isolated 2.7 g of a substance with m.p. 77-81° at 5 mm; n_D^{20} 1.4335.

b) To 10 g allylisopropenyl ketone (I) (b.p. 80-84° at 80 mm; n_D^{20} 1.4710) [1] was added 23 g 33% aqueous dimethylamine solution (heat was developed and the temperature rose to 61°). The mixture was then heated in a glass tube at 65° for 4 hours and then worked up as in the preceding experiment. The ethereal solution of organic bases was dried with magnesium sulfate and the product distilled in vacuum. 7.5 g of the above-described 2-methyl-5-dimethylamino-1-hexen-3-one (IV) was obtained. B.p. 98-100° at 14 mm; n_D^{20} 1.4560. The picrate melted at 119-120° (from alcohol).

c) A mixture of 30 g 1,5-dimethoxy-2-methylhexan-3-one (III) (b.p. 90-92° at 10 mm; n_D^{20} 1.4300) [1] and 60 g aqueous dimethylamine solution (33%) was heated in a sealed tube for 1.5 hours at 70° and the product worked up as in experiment a). The ethereal solution of the organic bases was dried with magnesium sulfate and distilled in vacuum. 16.2 g of 2-methyl-5-dimethylamino-1-hexen-3-one (IV) was obtained. B.p. 79-81° at 7 mm; n_D^{20} 1.4563.

The picrate melted at 119-120° and did not cause a depression in admixture with the preceding specimen.

Preparation of 1-methoxy-2-methyl-5-dimethylaminohexan-3-one (VII). A mixture of 40 g, 1,5-dimethoxy-2-methylhexan-3-one (III) and 20 ml dioxan, cooled to 0°, was saturated with gaseous dimethylamine (20 g

increase in weight). The mixture was then heated in a glass tube for 4 hours at 100° and then worked up as in the first experiment. 15.7 g of 1-methoxy-2-methyl-5-dimethylaminohexan-3-one (VII) was obtained in the form of a colorless liquid with a faint odor; b.p. 89-92° at 7 mm.

n_D^{20} 1.4420; d_4^{20} 0.9151; MR_D 54.10; calculated 53.96.

8.07 mg substance: 19;03 mg CO_2; 8.02 mg H_2O. 10.03 mg substance: 23.69 mg CO_2; 10.08 mg H_2O. Found %: C 64.43, 64.46; H 11.12, 11.25. $C_{10}H_{21}O_2N$. Calculated %: C 64.26; H 11.29.

This amino ketone does not give a picrate. From the neutral products was isolated 15 g of the original ketone with b.p. 84-87° at 6 mm; n_D^{20} 1.4320.

Preparation of 2-methyl-5-dimethylaminohexan-3-one (V). a) 10 g of the freshly distilled unsaturated amino ketone (IV) in solution in 20 ml ethanol was hydrogenated in presence of Pt-catalyst. The amount of hydrogen absorbed was 1.5 l (one molecule). 5.4 g of 2-methyl-5-dimethylaminohexan-3-one (V) was obtained in the form of a mobile liquid with an amine-like odor, turning yellow on standing. B.p. 70-72° at 12 mm.

n_D^{20} 1.4300; d_4^{20} 0.8537; MR_D 47.72; calculated 47.60.

4.225 mg substance: 0.340 ml N_2 (23°, 744 mm). 6.450 mg substance: 0.505 ml N_2 (22°, 749 mm). Found %: N 9.08, 8.96. $C_9H_{19}ON$. Calculated %: N 8.99.

Its picrate melts at 109-110° (from alcohol).

b) 14 g 2-methyl-5-methoxyhexan-3-one (VI) (b.p. 163-166° at 722 mm; n_D^{20} 1.4208) [1] and 35 g 33% aqueous dimethylamine solution were heated in a glass tube for 4 hours at 70°. The excess of dimethylamine was distilled off in vacuum on a water bath at 45°. The solution was treated with hydrochloric acid until weakly acid, the neutral products were extracted with ether (the amount of neutral products was extremely small). The organic base was salted out with potassium carbonate, extracted with ether, dried with sodium sulfate and fractionated in vacuum. 5.3 g of the above-described 2-methyl-5-dimethylaminohexan-3-one (V) was obtained. B.p. 73-75° at 14 mm; n_D^{20} 1.4301.

The picrate of this amino ketone melted at 108-110° and did not depress the melting point of the preceding specimen.

Preparation of 2-methyl-5-N-piperidyl-1-hexen-3-one (VIII). a) To 142 g 2-methyl-5-methoxy-1-hexen-3-one (II) was added 140 g piperidine and 40 g water. After addition of the water the temperature rose to 45°. The mixture was heated at 100° for 11 hours and then worked up as in previous experiments. 98 g 2-methyl-5-N-piperidyl-1-hexen-3-one (VIII) was obtained. B.p. 111-112° at 5 mm.

n_D^{20} 1.4810; d_4^{20} 0.9396; MR_D 59.08; calculated 58.91.

6.500 mg substance: 0.412 ml N_2 (23°, 769 mm). 4.804 mg substance: 0.304 ml N_2 (23°, 769 mm). Found %: N 7.40, 7.39. $C_{12}H_{21}ON$. Calculated %: N 7.18.

This amino ketone does not form a picrate.

b) To 18 g allylisopropenyl ketone (I) was added 35 g piperidine. The temperature of the reaction mass rose to 70°. After adding the piperidine the mixture was heated in a sealed tube for 4 hours at 70°, and then fractionated in vacuum to give 19 g amino ketone (VIII). B.p. 115-118° at 7 mm; n_D^{20} 1.4810.

c) 10 g 1,5-dimethoxy-5-methylhexan-3-one (III), 10 g piperidine and 5 ml water were heated for 2.5 hours at 100°. Unreacted piperidine (5.3 g) was distilled off in a low vacuum and the reaction mass worked up as in previous experiments. 5.2 g of the amino ketone (VIII) was obtained. B.p. 110-113° at 4 mm; n_D^{20} 1.4810.

Hydrogenation of 2-methyl-5-N-piperidyl-1-hexen-4-one. 10 g freshly distilled amino ketone (VIII) was hydrogenated in 15 ml alcohol with Pt-catalyst and absorbed 1.38 l of hydrogen (the theoretical amount). 6.7 g of 2-methyl-5-N-piperidylhexan-3-one (IX) was obtained. B.p. 79-80° at 9 mm.

n_D^{20} 1.4550; d_4^{20} 0.9004; MR_D 59.60; calculated 59.41.

4.04 mg substance: 0.285 ml N_2 (21°, 745 mm). 4.700 mg substance: 0.314 ml N_2 (21°, 740 mm). Found %: N 7.36, 7.18. $C_{12}H_{23}ON$. Calculated %: N 7.10.

This amino ketone does not form a picrate.

Preparation of 2-methyl-6-dimethylamino-2-hexen-4-one (XI). 50 g 2-methyl-6-methoxy-2-hexen-4-one (X) (b.p. 93-95° at 20 mm; n_D^{20} 1.4531) [2] and 75 g 33% aqueous dimethylamine solution were heated in an autoclave for 1 hour at 65°. The excess of dimethylamine was distilled off in vacuum on the water bath at 45°. The reaction mass was acidified with hydrochloric acid, extracted with ether, dried with sodium sulfate and distilled in vacuum to give 25 g of 2-methyl-6-dimethylamino-2-hexen-4-one (XI). B.p. 87-89° at 12 mm.

n_D^{20} 1.4600; d_4^{20} 0.9035; MR_D 47.00; calculated 47.24.

3.260 mg substance: 0.249 ml N_2 (20°, 734 mm). 2.950 mg substance: 0.229 ml N_2 (18°, 731 mm). Found %: N 8.56, 8.76. $C_9H_{17}ON$. Calculated %: N 8.99.

The picrate of the amino ketone (XI) melted at 106-107° (from alcohol). More prolonged heating lowers the yield of amino ketone (XI) and a considerable amount of a volatile mixture of products was obtained which was not further examined.

Preparation of 2-methyl-6-dimethylaminohexan-4-one (XII). a) 5.5 g freshly distilled unsaturated amino ketone (XI) in solution in 15 ml alcohol was hydrogenated in presence of Pt-catalyst when 883 ml hydrogen was absorbed (theory requires 878 ml). The catalyst was filtered off, the alcohol distilled off and the residue fractionated in vacuum to give 4.1 g 2-methyl-6-dimethyl-aminohexan-4-one (XII). B.p. 79-80° at 13 mm.

n_D^{20} 1.4318; d_4^{20} 0.8573; MR_D 47.71, 47.52.

4.110 mg substance: 0.326 ml N_2 (19°, 731). 5.595 mg substance: 0.431 ml N_2 (17°, 733). Found %: N 8.92, 8.74. $C_9H_{19}ON$. Calculated %: N 9.03.

The picrate forms flat needles melting at 99-100° (from alcohol).

b) 50 g 2-methyl-6-methoxyhexan-4-one (XIII) (b.p. 64° at 1[illegible] mm; n_D^{20} 1.4190) [2] and 78 g 33% aqueous dimethylamine solution were heated in an autoclave at 70° for 5 hours. The excess dimethylamine solution was heated in an autoclave at 70° for 5 hours. The solution was acidified with hydrochloric acid until weakly acid and the neutral products were extracted with ether. [illegible]

The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate and distilled in vacuum to give 24.2 g of amino ketone(XII). B.p. 83-84° at 14 mm; n_D^{20} 1.4315. Its picrate melts at 99-100° and does not depress the melting point of the preceding specimen.

10 g of the original methoxy ketone (XIII) was recovered from the neutral products. B.p. 64-65° at 11 mm; n_D^{20} 1.4201.

Preparation of 1,5-bis-dimethylaminohexan-3-one (XVI). 20 g of a mixture of the methoxy ketones (XIV) and (XV) (b.p. 83-87° at 9 mm; n_D^{20} 1.4330) [9] and 50 g 33% aqueous dimethylamine solution was heated at 60° for 3 hours. The excess of dimethylamine was then distilled off in vacuum on a water bath at 45°. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and distilled in vacuum to give 14.1 g 1,5-bis-dimethyl-aminohexan-3-one (XVI). B.p. 100-102° at 13 mm.

n_D^{20} 1.4563 d_4^{20} 0.9008; MR_D 56.30; calculated 56.26.

8.78 mg substance: 1.133 ml (20°, 753 mm). 4.79 mg substance: 0.615 ml (20°, 754 mm). Found %: N 14.90, 14.85. $C_{10}H_{22}ON_2$. Calculated %: N 15.05.

The picrate of the diamino ketone (XVI) melts at 145-146° (from alcohol).

Preparation of 1,5-bis-N-piperidylhexan-3-one (XVII). A mixture of 30 g methoxy ketones (XIV) and (XV) (b.p. 83-87° at 9 mm; n_D^{20} 1.4330 [10], 30 g piperidine and 10 g water was heated to 47° for 35 minutes. The product was then transferred to a glass ampoule and heated for 5 hours at 70°. The product was worked up as previously to give 25.3 g 1,5-bis-N-piperidylhexan-3-one (XVII). B.p. 98-100° at 4 mm.

n_D^{20} 1.4800; d_4^{20} 0.9537; MR_D 79.52; calculated 79.58.

2.563 mg substance: 0.235 ml N_2 (19.5°, 746 mm). 3.175 mg substance: 0.295 ml N_2 (19.5°, 746 mm). Found %: N 10.50, 10.64. $C_{16}H_{30}ON_2$. Calculated %: N 10.52.

The picrate of the diamino ketone (XVII), prepared by mixing with a saturated alcoholic solution of picric acid, melts at 134-135°.

3-Methyl-6-N-piperidyl-2-hepten-4-one (XXI). A mixture of 20 g 2-methoxy-5-methyl-5-hepten-3-one (XVIII) (B.p. 79-83° at 8 mm; n_D^{20} 1.4550) [10], 5 ml water and 20 g piperidine was heated in a sealed tube for 2.5 hours at 70°. The product was worked up as previously to give 8.2 g 3-methyl-6-N-piperidyl-2-hepten-4-one (XXI). B.p. 106-108° at 2 mm.

n_D^{20} 1.4830; d_4^{20} 0.9394; MR_D 63.63; calculated 63.51.

3.130 mg substance: 0.184 ml N_2 (20°, 748). 3.285 mg substance: 0.9052 ml N_2 (21°, 747). Found %: N 6.74, 6.78. $C_{13}H_{23}ON$. Calculated %: N 6.70.

This amino ketone does not form a picrate. From the neutral products was recovered 11.3 g methoxy ketone (XVIII). B.p. 67-80° at 8 mm; n_D^{20} 1.4730.

Hydrogenation of 3-methyl-6-N-piperidyl-2-hexen-4-one. 2.5 g of the freshly distilled amino ketone (XXI) dissolved in 15 ml alcohol was hydrogenated with Pt-catalyst and took up 300 ml hydrogen (as against the 280 ml required by theory). The catalyst was filtered off, the alcohol distilled off, and the product twice fractionated in vacuum to yield 1.2 g 3-methyl-6-N-piperidylheptan-4-one (XXII). B.p. 88-90° at 2 mm.

n_D^{20} 1.4704; d_4^{20} 0.9248; MR_D 63.69; calculated 63.98.

1.955 mg substance: 0.115 ml N_2 (21° 737 mm). 2.615 mg substance: 0.115 ml N_2 (21°, 734 mm). Found %: N 6.58, 6.43. $C_{13}H_{25}ON$. Calculated %: N 6.63.

The picrate came down as an oil which did not crystallize.

3-Methyl-6-dimethylamino-2-hepten-4-one (XIX). 18 g 2-methyoxy-5-methyl-5-hepten-3-one (XVIII). (B.p. 79-83° at 8 mm; n_D^{20} 1.4600) [10] and 40 g 33% aqueous dimethylamine solution were heated in an autoclave for 1.5 hours at 70°. After the usual treatment, the ethereal solution of the organic base was dried with sodium sulfate and distilled in vacuum. There was obtained 5.5 g of 3-methyl-6-dimethylamino-2-hepten-4-one (XIX). B.p. 70-72° at 4 mm.

n_D^{20} 1.4610; d_4^{20} 0.8982; MR_D 51.65; calculated 51.86.

13.17 mg substance: 3.76 ml 0.02 N $Na_2S_2O_3$. 20.78 mg substance: 6.05 ml 0.02 N $Na_2S_2O_3$. Found %: N 7.99, 8.01. $C_{10}H_{19}ON$. Calculated %: N 8.28

The picrate came down as an oil from various solvents and did not crystallize

Hydrogenation of 3-methyl-6-dimethylamino-2-hepten-4-one. 2.5 g of the freshly distilled amino ketone (XIX) in solution in 15 ml alcohol was hydrogenated in presence of Pt-catalyst for 9 hours, 300 ml hydrogen being taken up instead of the 330 ml theoretically required. The catalyst was filtered off, the alcohol distilled off and the residue fractionated in vacuum to give 1.2 g 3-methyl-6-dimethylamino-heptan-4-one (XX) with b.p. 62-64° at 2 mm.

n_D^{20} 1.4450; d_4^{20} 0.8731; MR_D 52.13; calculated 52.33

3.910 mg substance: 0.205 ml N_2 (16°, 763 mm). 4.870 mg substance: 0.318 ml N_2 (20°, 751 mm). Found %: N 7.73, 7.52. $C_{10}H_{21}ON$. Calculated %: N 8.17.

This amino ketone does not form a picrate.

Preparation of cyclohexenyl-β-dimethylaminopropyl ketone (XXIV). a) 14 g allyl-Δ'-cyclohexenyl ketone (b.p. 93-96° at 4 mm; n_D^{20} 1.5091) [11] and 50 g 33 % aqueous dimethylamine were energetically stirred at 70° for 4.5 hours (the initially homogeneous solution formed layers when heated). The excess of dimethylamine was removed in a vacuum on the water bath at 45°.

The solution was acidified with hydrochloric acid until acid, and the neutral products extracted with ether. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate and distilled in vacuum to give 10 g Δ'-cyclohexenyl-β-dimethylaminopropyl ketone (XXIV) in the form of a colorless liquid with a characteristic amine odor. B.p. 110-111° at 3 mm; n_D^{20} 1.5050; d_4^{20} 0.9664; MR_D 59.85; calculated 58.89.

The picrate of this amino ketone is a fine yellow powder. M.p. 163-164° (from alcohol).

8.30 mg substance: 3.90 ml 0.02 N $Na_2S_2O_3$. 7.50 mg substance: 3.54 ml 0.02 N $Na_2S_2O_3$. Found %: N 13.15, 13.21. $C_{18}H_{24}O_8N_4$. Calculated %: N 13.21.

b) 20 g β-methoxypropyl-Δ'-cyclohexenyl ketone (XXIII) (b.p. 102-104° at 4 mm; n_D^{20} 1.4870) [11] and 50 g 33% aqueous dimethylamine were heated in a glass tube for 3 hours at 70°. The reaction mixture was worked up as in the preceding experiment to give 10.3 g cyclohexenyl-β-dimethylaminopropyl ketone (XXIV) with b.p. 110-111° at 3 mm; n_D^{20} 1.5050. The picrate melted at 163-164° and did not depress the melting point of the previous sample. 7 g of the methoxy ketone (XXIII) was recovered from the neutral products. B.p. 100-103° at 3 mm; n_D^{20} 1.4863.

Hydrogenation of cyclohexenyl-β-dimethylaminopropyl ketone. 4.2 g of the freshly distilled amino ketone (XXIV) in solution in 20 ml alcohol was hydrogenated with Pt-catalyst. 575 ml hydrogen (550 ml is required by theory) was absorbed in the course of 8 hours, giving 1.3 g cyclohexyl-β-dimethylaminopropyl ketone (XXV) in the form of a transparent liquid with a faint amine odor. B.p. 80-82° at 2 mm.

n_D^{20} 1.4810; d_4^{20} 0.9453; MR_D 59.33; calculated 59.41.

3.216 mg substance: 0.204 ml N_2 (22°, 755 mm). 2.806 mg substance: 0.167 ml N_2 (23°, 750 mm). Found %: N 7.28, 6.77. $C_{12}H_{23}ON$. Calculated %: N 7.10.

This amino ketone does not give a picrate.

Cyclohexenyl-β-(N-piperidyl)-propyl ketone (XXVI). 20 g β-methoxypropylcyclohexenyl ketone (XXIII) (b.p. 102-104° at 4 mm; n_D^{20} 1.4870) [11] 5 ml water and 15 g piperidine were heated at 100° for 3 hours. The reaction mixture was then worked up in the usual way to give 12.3 g Δ'-cyclohexenyl-β-(N-piperidyl)-propyl ketone (XXVI) in the form of a thick liquid with b.p. 114-116° at 4 mm; n_D^{20} 1.5150. Its picrate forms fine golden needles melting at 118-119° (from alcohol).

6.595 mg substance: 0.706 ml N_2 (23°, 747 mm). 9.172 mg substance: 0.961 ml N_2 (22°, 745 mm). Found %: N 12.14, 11.89. $C_{21}H_{28}O_8N_4$. Calculated %: N 12.07.

SUMMARY

An aqueous solution of dimethylamine acts on allylisopropenyl ketone (I) and the methoxy ketones (II, III) to form, in good yield, the amino ketone (IV), which takes up one molecule of hydrogen when hydrogenated and gives the saturated amino ketone (IV). This amino ketone is also obtained by the action of dimethylamine on the saturated methoxy ketone (VI). Anhydrous dimethylamine reacts with the dimethoxy ketone (III) to give the methoxyamino ketone (VII).

Aqueous solutions of piperidine act on the dienone (I) and the methoxy ketones (II, III) to form the amino ketone (VIII), which absorbs one molecule of hydrogen on hydrogenation and forms the saturated amino ketone (IX).

Dimethylamine reacts with the methoxy ketone (X) to give a good yield of the amino ketone (XI), which absorbs one molecule of hydrogen when hydrogenated and forms the saturated amino ketone (XII); the latter is also obtained by the action of dimethylamine on the saturated methoxy ketone (XIII).

Reaction of dimethylamine with the methoxy ketones (XIV, XV) gives the diaminoketone (XVI), and with piperidine the same methoxy ketones give the diaminoketone (XVII).

Dimethylamine acts on the methoxy ketone (XVIII) to form the amino ketone (XIX), which on hydrogenation forms the saturated amino ketone (XX). Piperidine reacts with the methoxy ketone (XVIII) to form the amino ketone (XXI), which on hydrogenation forms the saturated amino ketone (XXII).

Dimethylamine acts on the methoxy ketone (XXIII) to give the amino ketone (XXIV), which hydrogenates to the saturated amino ketone (XXV), while piperidine with the methoxy ketone (XXIII) gives the amino ketone (XXVI).

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Received December 19, 1950

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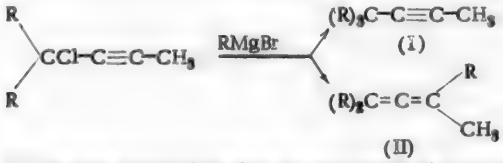
INTRAMOLECULAR REARRANGEMENTS IN THE ACETYLENE SERIES

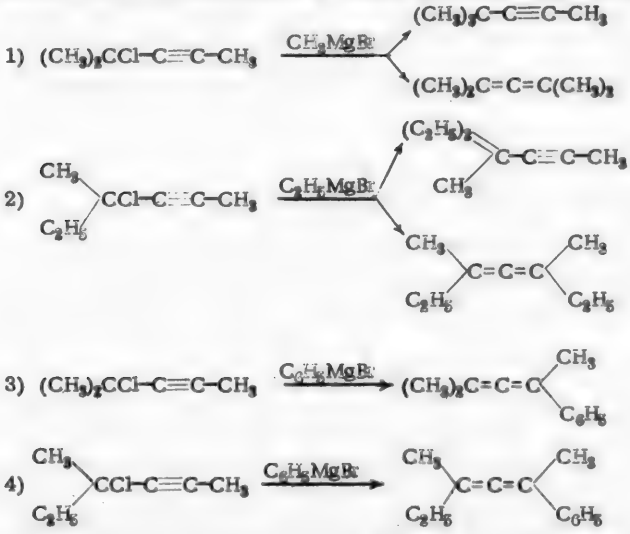
VII. REACTION OF 2,2,3-TRIMETHYL-3-CHLOROHEXYNE-4 WITH ORGANOMAGNESIUM COMPOUNDS

A. I. Zakharova and R. A. Sapozhnikova

In previous communications [1,2] on the study of the interaction of acetylenic tertiary chlorides of the type of $(R)_2CCl-C\equiv C-CH_3$ with organomagnesium compounds it was pointed out by one of us that the reaction is complex and that its products, apart from the corresponding acetylenic hydrocarbons with a quaternary carbon atom (I), are isomeric hydrocarbons with an allene structure (II):



It was also established that the direction of the reaction was influenced by the character of the organomagnesium compound. In the reaction of acetylenic chlorides with RMgBr (where R = CH_3 or C_2H_5) there is formed a mixture of two hydrocarbons: an acetylenic one (I), the product of normal substitution of chlorine for the radical of the organomagnesium compound, and an allenic one (II), whose formation is only possible when intramolecular rearrangement takes place in the instant of reaction (equations 1 and 2). In the case, however, of reaction of the chloride with C_6H_5MgBr the reaction proceeds exclusively in the second direction with formation only of a tetrasubstituted allenic hydrocarbon (equations 3 and 4):



Continuing our investigations in this direction, we decided to examine other examples of this phenomenon. From this standpoint we performed reactions between an acetylenic tertiary chloride—2,2,3-trimethyl-3-chlorohexyne-4 (III)—and organomagnesium compounds (CH_3MgBr and C_6H_5MgBr). The reactions were conducted in the conditions described in previous papers [1,2]. After appropriate treatment of the reaction mass obtained by reaction of the chloride (III) with CH_3MgBr, a hydrocarbon whose physical constants are listed in Table 2 was obtained in 73% of the theoretical yield. The molecular weight and elementary analysis of the product correspond to the formula $C_{10}H_{18}$. It does not react with maleic anhydride. The Raman spectrum of this hydrocarbon was plotted. As Table 1 shows, the spectrum contains strong lines corresponding to the characteristic frequencies of the triple bond (2225 and 2261 cm^{-1}) and of the double bond (1638 cm^{-1}).

TABLE 1

Raman Spectrum of the Product of Interaction of the Chloride (III) with CH_3MgBr.

386 (1), 420 (2), 446 (2), 551 (2), 578 (2), 621 (5), 745 (3), 852 (3), 922 (4), 1028 (2), 1066 (2), 1132 (2), 1202 (2), 1230 (2), 1255 (2), 1383 (4), 1447 (4), 1603 (2), **1638 (4), 2225** (4), 2261 (3).

The presence in the spectrum of a line characteristic of compounds containing an acetylenic linkage pointed to formation of a product of the normal reaction—the acetylenic hydrocarbon 2,2,3,3-tetramethylhexyne-4 (IV), but on the other hand the spectrum clearly indicated that an acetylenic hydrocarbon was not the sole product.

The product was oxidized with alkaline permanganate with cooling. The oxidation did not quite proceed on the usual lines. At first it proceeded very readily, but later the solution became decolorized although less oxidizing agent had been consumed than was required by calculation.* Oxidation was stopped. Examination of the neutral products revealed the formation of acetone and pinacoline. This pointed to the presence in the investigated hydrocarbon mixture of a tetrasubstituted allene—2,2,3,5-tetramethylhexadiene - 3,4 (V). A minute amount of acetic acid was identified in the acidic products of oxidation.

Apart from acetone and pinacoline, another product was isolated from the alkaline solution which proved on closer examination (molecular weight determination, elementary analysis) to be the hydrocarbon $C_{10}H_{18}$. Its composition therefore corresponded to the composition of the product subjected to oxidation, but it differed considerably in physicochemical properties (Table 2).

TABLE 2

Substance	Constants				
	B.p.	d_4^{20}	n_α^{20}	MR_α	Relative dispersion, $\omega_{\alpha\beta}$
Hydrocarbon mixture subjected to oxidation	47° at 15 mm	0.7794	1.4416	46.81	22.2
Hydrocarbon recovered from the oxidation products	50-51.5° at 25 mm	0.7932	1.4369	45.61	18.83

Particularly conspicuous is the sharp reduction in relative dispersion of the hydrocarbon recovered from the oxidation products; according to the literature the relative dispersion of 18.8 corresponds to a hydrocarbon with a triple bond [3]. This consideration, as well as the fact that we failed to find dimethyl tert. butylacetic acid in the acid oxidation products whereas this acid should be formed by oxidation of the acetylenic hydrocarbon (IV), led us to conclude that it was this hydrocarbon which was recovered since it was the more difficult to oxidize.

There is evidence in the literature pointing to the difficulty of oxidizing hydrocarbons with approximately the structure in question. Thus, for instance, in the oxidation with alkaline permanganate solution of di-tert-butylacetylene by Hennion and Banigan [4], instead of the anticipated trimethylacetic acid, ditertbutyl ketone was obtained, and no further oxidation occurred.

$$(CH_3)_3C{-}C{\equiv}C{-}C(CH_3)_3 \longrightarrow (CH_3)_3C{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}C(CH_3)_3$$

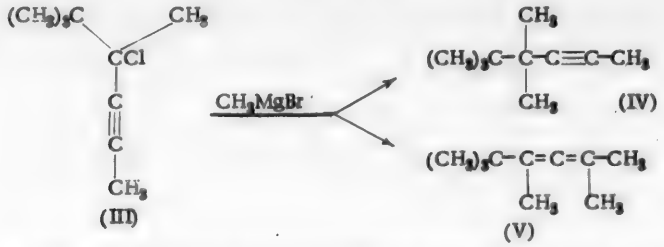
In this respect such hydrocarbons behave to some extent like disubstituted acetylenic hydrocarbons containing triphenylmethyl groups, which are known to be exceptionally stable [5].

Unfortunately, due to the very small amount of the hydrocarbon recovered from the oxidation products, we were unable conclusively to establish its structure. But all the data set out above point in all probability to the presence of an acetylenic hydrocarbon formed by the normal reaction of chloride (III) with CH_3MgBr. In this case, therefore, by sacrificing one of the hydrocarbons of the investigated mixture—the tetrasubstituted allene (V) which was oxidized to acetone and pinacoline—we were able to isolate the second hydrocarbon—the disubstituted acetylene (IV).

Thus, in this case also, we have been able to demonstrate that the reaction between tertiary acetylenic

* The amount of oxidizing agent used was calculated on the assumption that the acetylenic and allenic hydrocarbons were present in equal amounts.

chlorides and organomagnesium compounds leads to formation of two hydrocarbons: The product of normal substitution, a disubstituted acetylene, and the product of an anomalous reaction, a tetrasubstituted allene.



A study was also made of the reaction of chloride (III) with C_6H_5MgBr. This reaction gave a hydrocarbon whose elementary analysis and molecular weight corresponded to the formula $C_{15}H_{20}$. Oxidation with alkaline permanganate solution yielded pinacoline, acetophenone and a small amount of benzoic acid. The very same products were obtained by ozonolysis of the hydrocarbon.

The Raman spectrum of this hydrocarbon was plotted. As shown in Table 3, the spectrum contains strong lines in the region of the characteristic frequencies 1604 and 1598 cm^{-1}. The doublet~1600 cm^{-1} is evidence, as we know [6], of the presence of a benzene ring. No lines were observed in the region characteristic of the acetylenic bond.

TABLE 3

Raman Spectrum of the Product of Reaction of the Chloride (III) with C_6H_5MgBr.

400 (1), 550(1), 621 (1), 643 (1), 790 (1), 874 (1), 998 (5), 1028(1), 1154 (1), 1254 (1), 1274 (1), 1378 (0.5), 1444 (0.5), **1598** (5), **1604** (4).

The spectrographic data for the hydrocarbon in question permits the conclusion that it does not contain a a triple bond, while the formation during oxidation and ozonolysis of only pinacoline and acetophenone demonstrates that the reaction proceeds entirely with molecular rearrangement according to the scheme:

with formation of the tetrasubstituted allene, 2,2,3-trimethyl-5-phenylhexadiene-3,4 (VI).

Thus it has once again been shown that the character of the organomagnesium compound influences the result of the reaction. Formation of the normal reaction products – disubstituted acetylenic hydrocarbons with a quaternary carbon atom of the type of (I) – is evidently hindered by steric hindrance when a phenyl radical is present in the organomagnesium compound.

In conclusion it must be noted that both in this investigation and in earlier ones [1,2] on the reaction of acetylenic tertiary chlorides with organomagnesium compounds as represented in equations 1-4, we have demonstrated the formation of acetylenic hydrocarbons with a quaternary carbon atom (I) both by the chemical and spectrographic method. On the other hand the formation in this reaction, side by side with acetylenic hydrocarbons, of allenic hydrocarbons (II), has only been chemically demonstrated, namely by the preparation of the corresponding ketones by oxidation and ozonolysis. There are no strong lines in the ~1070 cm^{-1} region of the Raman spectra of the investigated hydrocarbon mixtures, i.e. the region of frequencies characteristic of the allene linkage, according to the literature [7]. On the other hand in all cases strong lines characterizing the frequency of the double bond, i.e. ~1640 cm^{-1}, were observed. In this connection it may be suggested that the reaction products contain hydrocarbons with a conjugated system of double bonds. In the present investigation, for example, the appearance of acetone and pinacoline during oxidation of the product of reaction of chloride (III) with CH_3MgBr might be explained by the simultaneous presence of two hydrocarbons containing a conjugated system of double bonds (VII) and (VIII): *

* This hypothesis is supported by the presence of acetic acid in the oxidation products.

These hydrocarbons could have been formed by subsequent isomerization of the initially formed allene hydrocarbon (V), but our attempts to demonstrate the presence of the latter by chemical methods, e.g, by forming condensation products with maleic anhydride, led, as stated above, to negative results.

On the other hand, it is still difficult at the present time to draw a final conclusion from the Raman spectra because the spectra of tetrasubstituted allenes have not been described in the literature, evidently due to their difficult availability. Concerning the Raman spectra of other allenic hydrocarbons, they too have been inadequately investigated and in some cases even with conflicting results. For example, whereas methylallene [9] and symm. dimethylallene [10] exhibit a characteristic frequency of $\sim$1071 cm^{-1}, this frequency is absent from the spectrum of asymm. dimethylallene [9]. Again, the spectrum of ethylallene [10] contains the frequency of 1640 cm^{-1} which is not inferior in intensity to the frequencies 1062 and 1098 cm^{-1}.

EXPERIMENTAL

The starting acetylenic chloride 2,2,3-trimethyl-3-chlorohexyne-4 was prepared by the action of hydrogen chloride on methyl-tert-butylmethylethinyl carbinol, which in turn was synthesized by the Favorsky reaction from pinacoline and methylacetylene. The constants of both substances corresponded to those enumerated in a paper by one of us and K. N. Dobromyslova [8].

1. Reaction of 2,2,3-trimethyl-3-chlorohexyne-4 with CH_3MgBr

The Grignard reagent was prepared from 12 g magnesium and 67 g methyl bromide in 150 ml ether. During the addition of the chloride (III) (44 g in 100 ml ether) the mixture was rapidly stirred and cooled with cold water. The complex was left overnight and then decomposed with 6% hydrochloric acid solution with external cooling to 0°. The ethereal solution was dried with $MgSO_4$, the ether driven off, and the residue fractionated in vacuum to give the following fractions: 1) B.p. 47° at 15 mm; 2) b.p. 47-53° at 15 mm. The yield of the first fraction was 73%. The prepared hydrocarbon was a colorless, transparent liquid.

d_4^0 0.7953; d_4^{20} 0.7794; n_α^{20} 1.4416; n_β^{20} 1.45143; MR_α 46.81; MR_β 47.71. $C_{10}H_{18}$. Calculated MR_α 46.11; MR_β 46.95. $C_{10}H_{18}$. Calculated MR_α 47.15; MR_β 48.09. Relative dispersion $\omega_{\alpha\beta}$ 22.2.

0.3418 g substance: 22.27 g benzene: Δt 0.57°. 0.1517 g substance; 22.27 g benzene: Δt 0.25°. 0.0710 g substance: 0.2253 g CO_2; 0.0826 g H_2O. 0.0673 g substance: 0.2140 g CO_2; 0.0771 g H_2O. Found %: C 86.54, 86.72; H 13.01, 12.82; M 134.6, 136.2. $C_{10}H_{18}$. Calculated %: C 86.96; H 13.04; M 138.

Oxidation. In order to investigate the structure 10 g of the hydrocarbon was oxidized with 1% alkaline $KMnO_4$ solution. Oxidation at first proceeded very readily, but after 19.1 g of oxidizing agent had been added the solution became colorless. The calculated requirement for complete oxidation of 10 g of the mixture of hydrocarbons was 26.7 g $KMnO_4$. The alkaline solution together with the manganese dioxide precipitate was transferred to a flask for distillation of the neutral products. The liquid in the receiver separated into two layers: an upper one of greenish liquid and a lower aqueous layer. The latter was separated and again distilled. The first drops of distillate were collected in a solution of p-nitrophenylhydrazine acetate. A precipitate came down which after recrystallization from methanol had m.p. 146-148° and did not depress the melting point of authentic acetone p-nitrophenylhydrazone.

0.0465 g substance: 8.8 ml N_2 (20°, 759.4 mm). 0.0384 g substance: 7.4 ml N_2 (20°, 751.5 mm). Found %: N 21.72, 21.87. $C_9H_{11}O_2N_3$. Calculated %: N 21.76.

The upper layer (about 2 g) was distilled into a solution of semicarbazide acetate. A precipitate formed and a layer of greenish liquid again collected in the mother liquor. The precipitate was recrystallized from methanol and had m.p. 156°. It did not depress the melting point of pinacoline semicarbazone.

0.0502 g substance: 11.5 ml N_2 (19°, 753.7 mm). 0.0552 g substance: 12.4 ml N_2 (18°, 770.4 mm). Found %: N 26.23, 26.36. $C_7H_{15}ON_3$. Calculated %: N 26.75.

The layer of greenish liquid was separated from the semicarbazide mother liquor, dried over $MgSO_4$ and distilled. A fraction boiling at 50-51.5° at 25 mm was collected. Since the liquid was colored, it was transferred to a bulb for further purification. The air was removed from the bulb which was then sealed, and the liquid was subjected to molecular distillation to give a transparent liquid with a faint yellow-green tint. It was impossible to determine its specific gravity at 0° because the substance crystallized at this temperature.

d_4^{20} 0.7932; n_α^{20} 1.43696; n_β^{20} 1.44519; MR_α 45.61; MR_β 46.35. $C_{10}H_{18}$. Calculated MR_α 46.11; MR_β 46.95. Relative dispersion $\omega_{\alpha\beta}$ 18.83.

0.1240 g substance: 0.3958 g CO_2: 0.1421 g H_2O. 0.0610 g substance; 19.85 g benzene: Δt 0.115°. 0.1296 g substance: 17.25 g benzene: Δt 0.275°. Found %: C 87.05; H 12.82; M 133.6, 136.6. $C_{10}H_{18}$. Calculated %: C 86.96; H 13.04; M 138.

On the basis of the analytical results we can assume with a high degree of probability that one of the components of the hydrocarbon mixture subjected to oxidation was unaffected by the oxidizing agent and was recovered unchanged. The molecular refraction and relative dispersion indicated that this hydrocarbon was an acetylene derivative.

After distilling off the neutral products, the precipitate of manganese dioxide was filtered off, and the solution concentrated prior to acidification with sulfuric acid. Several fractions of 15 ml each were collected on distilling the volatile acids. Silver salts were prepared by treatment with silver carbonate and were identified as silver acetate.

0.0833 g substance: 0.0536 g Ag. 0.0222 g substance: 0.0143 g Ag. Found %: Ag 64.34, 64.40. $C_3H_3O_2Ag$. Calculated %: Ag 64.67.

2. Reaction of 2,2,3-Trimethyl-3-chlorohexyne-4 (III) with C_6H_5MgBr

The organomagnesium compound prepared from 9 g magnesium and 55 g bromobenzene in 200 ml ether was decanted from the magnesium residue and to it was added dropwise, with rapid stirring, 44.5 g chloride (III) (0.35 mole) in 100 ml ether. The reaction proceeded quietly. After the whole of the chloride had been added, the solution was stirred for another 2 hours with heating on the water bath (40°). On the following day the complex was decomposed with 6% hydrochloric acid while being stirred and externally cooled to 0°. The ethereal solution was dried with $MgSO_4$. Fractionation of the reaction product over metallic sodium yielded two fractions: 1) B.p. 56-60° at 30-34 mm; 2) b.p. 118-119° at 10 mm. Due to its very small quantity the first fraction was not investigated. The second fraction was redistilled to give a hydrocarbon with b.p. 111-112° at 6 mm. Yield 36% of theory.

d_4^0 0.9265; d_4^{20} 0.9101; n_D^{20} 1.53353; n_α^{20} 1.53060; n_β^{20} 1.54968; MR_D 68.49; MR_α 67.92; MR_β 69.97. $C_{15}H_{20}$. Calculated MR_D 66.93; MR_α 66.48; MR_β 67.99.

0.0955 g substance: 0.3135 g CO_2; 0.0846 g H_2O. 0.0814 g substance: 0.2673 g CO_2; 0.0731 g H_2O. 0.1098 g substance; 17.4 g benzene: Δt 0.16°. 0.3178 g substance; 17.55 g benzene: Δt 0.46°. Found %: C 89.52, 89.65; H 9.90, 10.05; M 197.1, 196.8. $C_{15}H_{20}$. Calculated %: C 90.0; H 10.0, M 200.

Ozonization. 3.3 g of the hydrocarbon was ozonized in chloroform solution until ozone absorption had ceased. The chloroform was removed in vacuum and the ozonides decomposed by boiling with water. The odor of pinacoline was detected on distilling the first drops of the neutral ozonolysis products with steam, but we were unable to isolate the substance owing to the small quantity. The oil which collected in the receiver was separated from water and dried; it was then treated with a solution of semicarbazide acetate when a precipitate came down which after recrystallization melted at 197-198° and did not depress the melting point of acetophenone semicarbazone.

0.0908 g substance: 18.7 ml N_2 (19°, 764.5 mm). Found %: N 23.88. $C_9H_{11}ON_3$. Calculated %: N 23.73.

The solution remaining after distillation of the neutral products was acidified with sulfuric acid. On distillation of the acid products, white crystals were collected which after drying and sublimation melted at 119-120° and did not depress the melting point of benzoic acid. No other acids were detected.

Oxidation. 6.25 g of the hydrocarbon was taken for oxidation. This was performed with 1% alkaline solution of $KMnO_4$ in amount calculated for the expenditure of 4 atoms of oxygen per molecule of hydrocarbon. A two-layer liquid was collected on distilling the neutral products of oxidation. The top layer (a yellow oil) was separated from the water and distilled into a solution of semicarbazide acetate. The first drops, b.p. 105-110°, were collected separately. Semicarbazones were prepared from each fraction. The semicarbazone of the first fraction melted at 154-156° (from methanol) and did not depress the melting point of pinacoline semicarbazone.

0.0586 g substance: 13.6 ml N_2 (21°, 770.4 mm). Found %: N 26.91. $C_7H_{15}ON_3$. Calculated %: N 26.75.

The semicarbazone of the second fraction melted at 197-198° after recrystallization and did not depress the melting point of acetophenone semicarbazone.

0.0541 g substance: 11.1 ml N_2 (17.5°, 761.6 mm). Found %: N 23.90. $C_9H_{11}ON_3$. Calculated %: N 23.73.

The precipitate of manganese dioxide was filtered off after distillation of the neutral products and the solution was acidified with sulfuric acid and distilled. Crystals formed in the condenser and melted at 118-120° after drying and sublimation. They did not depress the melting point of benzoic acid.

SUMMARY

1. The reaction of the tertiary acetylenic chloride, 2,2,3-trimethyl-3-chlorohexyne-4 (III), with organomagnesium compounds was investigated.

2. It was shown that the reaction of chloride (III) with CH_3MgBr is accompanied by intramolecular rearrangement with the consequence that in addition to the normal reaction product – the disubstituted acetylenic hydrocarbon with a quaternary carbon atom, 2,2,3,3-tetramethylhexyne-4 (IV) – there is formed an anomalous reaction product in the shape of the tetrasubstituted allene, 2,2,3,5-tetramethylhexadiene-3,4 (V).

3. Reaction of the chloride (III) with C_6H_5MgBr only gave the anomalous product – the tetrasubstituted allene, 2,2,3-trimethyl-5-phenylhexadiene-3,4 (VI).

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Received April 17, 1951

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•• See Consultants Bureau translation, p. 2099.

CONDENSATION OF FORMALDEHYDE WITH KETONES AND ALDEHYDES

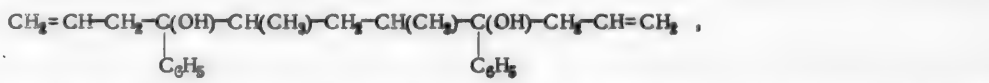
SYNTHESIS OF 5,7-DIMETHYL-4,8-DIPHENYLUNDECADIENE-1,10-DIOL-4,8

N. K. Astakhova and M. N. Tilichenko

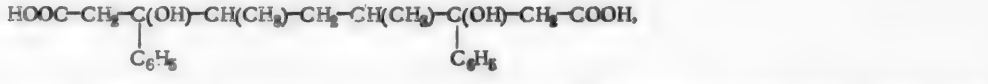
In a recent communication [1] we described a convenient preparative synthesis of methylene-bis-propiophenone ($C_6H_5COCH(CH_3)CH_2CH(CH_3)COC_6H_5$), by condensation of propiophenone with formaldehyde. This delta-diketone is obtained in the form of a crystalline compound (in quantity of about one-third of the total mass of product) and in the form of a yellow syrup (about two-thirds). We suggested [1] that these were stereoisomers, the first probably being the inactive form and the second the racemate.

In the present paper we describe the reaction of the crystalline and liquid forms of methylene-bis-propiophenone with allyl iodide and magnesium by the Yavorsky method [2] as modified by Mazurevich [3].

The reaction with both the crystalline and the liquid methylene-bis-propiophenone gave a quantitative yield of



5,7-dimethyl-4,8-diphenylundecadiene-1,10-diol-4,8, in the form of a semisolid syrup. Oxidation of the glycol gave a dibasic acid in the form of a white, amorphous powder,



4,6-dimethyl-3,7-diphenyl-3,7-dihydroxynonane dicarboxylic acid, the structure of which was confirmed by analysis of its silver salt.

The first and second compounds each contain four asymmetric carbon atoms and they are consequently a mixture of several stereoisomeric forms (which evidently explains why at first we were unable to obtain them in crystalline form).

EXPERIMENTAL

The reaction with crystalline and liquid methylene-bis-propiophenone was performed in completely identical conditions: To 4.28 g (0.178 mole) freshly prepared magnesium turnings, covered with 75 ml absolute ether, was added about 2 ml freshly distilled allyl iodide (b.p. 99-103°), to "activate" the turnings, and the mixture heated on the water bath for 30-40 minutes. Addition was then made in small portions, with mechanical stirring, of 20 g (0.07 mole) diketone and 30 g (0.178 mole) allyl iodide dissolved in 40 ml absolute ether. The reaction flask was cooled the whole time with a cold-water bath, since the process proceeds too energetically without cooling, even with very slow addition of the reagents.

On the following day the reaction mass was treated first with aqueous ether, then with iced water and hydrochloric acid. The ether layer was separated and the aqueous layer extracted several times with fresh portions of ether. The ether extracts were combined with the ether layer and the whole washed with water until it gave a negative reaction for halogen. After drying with freshly calcined sodium sulfate, the ether was distilled off on the water bath and the flask residue brought to constant weight in a vacuum (1-2 mm) at 50-60°. The so-obtained product was a soft, vitreous mass (a thread-forming syrup) with the color of tea. In the reaction with the crystalline diketone the yield was 25.2 g or 97.8% of the theoretical; with the liquid diketone it was 24.63 g or 94.6%.

The substance distilled in vacuum (less than 1 mm) at 210-227° (with decomposition). With Deniges'

reagent [4] it gives a characteristic precipitate, typical of compounds with double bonds and tertiary alcoholic groups. It is readily soluble in all common solvents except water. It has a pleasant mushroomy odor.

0.1131 g substance: 3420 g CO_2; 0.0953 g H_2O. 0.1198 g substance: 0.4259 g CO_2; 0.1132 g H_2O. 0.1218 g substance: • 0.3654 g CO_2; 0.0905 g H_2O. Found %: C 82.50, 81.94 , 81.89; H 9.40, 9.05, 8.31. $C_{25}H_{32}O_2$. Calculated %: C 82.37; H 8.85. 0.2856 g substance; 16.63 g benzene: Δt 0.256°. 0.2660 g substance; 14.48 g benzene: Δt 0.267° 0.2824 g substance: 16.37 g benzene; Δt 0.225°. Found: M 351.4, 360.7, 352.3. $C_{25}H_{32}O_2$. Calculated: M 364.5. Iodine value (McIlheny's method) 0.2714 g substance: 28.14 ml 0.1 N $Na_2S_2O_3$. 0.2366 g substance 24.00 ml 0.1 N $Na_2S_2O_3$. 0.2961 g substance • 32.28 ml 0.1 N $Na_2S_2O_3$. Found: iodine value 133.3, 132.7,138.5. $C_{25}H_{32}O_2$. Calculated: iodine value 132.28. 0.1696 g substance: 22.5 ml CH_4 (22°, 750 mm) (Terentyev) 0.1853 g substance: 26.1 ml CH_4 (23°, 750 mm). 0.1525 g substance: • 20.5 ml CH_4 (19.5°, 746.5 mm). Found %: OH 9.01, 9.51, 9.20. $C_{25}H_{32}O_2$. Calculated %: OH 9.33.

Oxidation. Oxidation was effected by the method described by Chojn [5]. The amount of oxidizing agent used was calculated on the assumption that 1 mole of substance required 8 atoms of oxygen.

5 g unsaturated glycol was dissolved in 50 ml acetone, a little water was added and the whole thoroughly emulsified. To the emulsion, cooled in a bath containing iced water, was added with good stirring a 4 % $KMnO_4$ solution (12.1 g in 290 ml water) in small portions, also cooled with cold water. Decolorization of the permanganate took place fairly quickly. After the whole of the permanganate had been added, the excess was reduced by careful addition of a small amount of formaldehyde. The mixture was filtered and the precipitate together with the filter was transferred to a conical flask and digested several times with fresh portions of water. The filtered liquors were combined with the main filtrate and evaporated in a moderate vacuum at 70-80° approximately to a volume of 120 ml. The concentrated solution was extracted several times with ether to remove the neutral products. The clear liquid left after the ether treatment was acidified with 10% hydrochloric acid; an emulsion was formed which deposited a yellow oil. The oil was extracted with ether several times. The ether extract was washed with water several times until it gave a negative reaction for chlorine and dried with freshly calcined sodium sulfate. The ether was driven off and the residue brought to constant weight in vacuum at 50-60°. Yield of acid 2.5 g or 45.6% of theory.

The acid, in the form of a faintly yellow powder, is soluble in alcohol, ether, benzene, slightly less soluble in carbon tetrachloride and carbon bisulfide, and completely insoluble in water and gasoline (b.p. 80-100°). M.p. 63-67°. The acid could not be obtained in the crystalline form.

Preparation and analysis of the Ag salt. The acid was dissolved in concentrated ammonia by heating (dissolution takes place very slowly in the cold; it is also slow in dilute ammonia). The solution was heated until the ammonia had been completely driven off, filtered from a small amount of brown flocculent suspension, and precipitated with concentrated silver nitrate solution. A white, curdy precipitate of the silver salt immediately came down. It was sucked dry on a glass filter, washed with alcohol and water until it had a negative reaction for silver ions, and dried to constant weight at 80° (at 90-100° it decomposes appreciably).

0.2766 g substance: 0.0970 g Ag. Found %: Ag 35.07. $C_{23}H_{26}O_6$. Calculated %: Ag 35.13.

SUMMARY

1. It is shown that methylene-bis-propiophenone is an excellent component for the organomagnesium synthesis.

In its reaction with allyl iodide and magnesium, the process proceeds normally to form, in quantitative yield, 5,7-dimethyl-4,8-diphenylundecadien-1,10-diol-4,8, not described in the literature.

Oxidation of the unsaturated glycol yielded 4,6-dimethyl-3,7-diphenyl-3,7-dihydroxynonane dicarboxylic acid, not described in the literature.

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Received January 23, 1951

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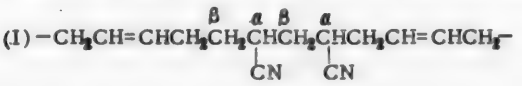
• Data for the same product obtained on the basis of the liquid methylene-bis-propiophenone.

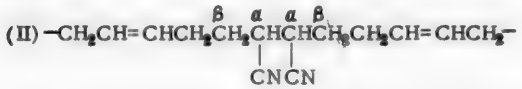
THE PROBLEM OF THE STRUCTURE OF THE COPOLYMER OF BUTADIENE AND ACRYLONITRILE

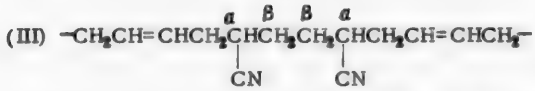
SYNTHESIS OF HEXANETETRACARBOXYLIC ACID

E. N. Alekseeva and V. D. Mezhov

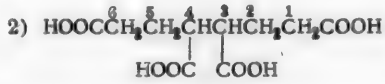
In 1939 one of the authors [1] published a paper on the elucidation of the structure of the copolymer of butadiene and acrylonitrile by the ozonization method. The main product of cleavage was isolated in the form of the trimethyl ester of 1,2,4-butanetricarboxylic acid. The properties of the free acid obtained by saponification of the trimethyl ester agreed completely with those of Ruzicka's preparation [2]. In addition to butantricarboxylic acid the ozonization products included a small amount of the tetramethyl ester of hexanetetracarboxylic acid whose structure could not be confirmed owing to the inadequate amount of material. The formation of hexanetetracarboxylic acid indicates that in the process of polymerization, apart from the regular successive alternation of molecules of butadiene and acrylonitrile, addition may take place between two molecules of acrylonitrile. There are three possible ways in which this addition could occur:

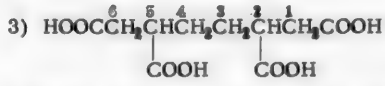






Oxidative cleavage could correspondingly yield three different hexanetetracarboxylic acids:





In order to establish which of the three possible hexanetetracarboxylic acids actually corresponds to the structure of the acid derived from the copolymer, all three isomers have been synthesized. Comparison of the properties of the acid isolated from the copolymer with those of the synthesized acids showed that it was identical with 1,2,4,6-hexanetetracarboxylic acid. Consequently in the successive addition of two molecules of acrylonitrile between themselves, the α-carbon atom of one molecule adds on to the β-carbon atom of the other (I).

A new original method was developed for preparation of the ester of β-bromopropionic acid used as intermediate. This method involved acting with dry hydrogen bromide on an alcoholic solution of acrylonitrile with intermediate formation of the hydrobromide of the imino ester.

EXPERIMENTAL

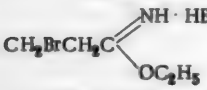
All the condensation reactions were carried out in a three-necked flask equipped with a mechanical

stirrer with a mercury seal, a dropping funnel and a reflux condenser topped by a calcium chloride tube. Sodium ethylate was first prepared and to this was added an ester with a mobile hydrogen atom. The reaction mixture was stirred for a short period, after which the second reaction component was added. At the end of the reaction the alcohol was distilled off under reduced pressure, the reaction mass was decomposed with water and extracted with ether, and the ether extract dried with calcium chloride. After distilling off the ether, the residue was fractionated in vacuum.

Preparation of the triethyl ester of 1,1,3-propanetricarboxylic acid. 8.74 g metallic sodium (0.38 g-atom) is dissolved in 95 ml absolute alcohol. To the solution of ethylate is added 61 g freshly dissolved ethyl maleate (0.38 mole). The resultant sodium ethyl malonate is cooled with ice and to it is added dropwise 50 g of the ethyl ester of β-bromopropionic acid (0.28 mole). The reaction mass is stirred for an hour at room temperature. After the treatment described above and fractionation under reduced pressure, the yield of triethyl ester of 1,1,3-propanetricarboxylic acid with b.p. 136° at 4 mm was 42 g (57.5%), and that of the tetraethyl ester of 1,3,3,5-pentanetetracarboxylic acid with b.p. 187° at 4 mm was 14 g (28%).

Synthesis of the ethyl ester of β-bromopropionic acid. 53 g acrylonitrile (1 mole) is dissolved in 150 ml ethyl alcohol (2.6 mole). Under ice cooling the solution is saturated with dry hydrogen bromide until the weight had increased to 160 g and the mass left overnight.

On the following day the hydrobromide of the imino ester of β-bromopropionic acid,



, crystallized. After driving off the alcohol the amount of crystals increased. The crystalline mass was decomposed with water, the resultant colorless oil was distilled under reduced pressure. B.p. 64-65° at 5 mm. Yield 98-102 g (54-56 %).

The hydrobromide of the imino ester of β-bromopropionic acid crystallizes in the form of stout prisms; readily soluble in hot alcohol, sparingly soluble in cold. If thoroughly washed free of mother liquor, it may be kept for several days in the dark in a desiccator over calcium chloride. In the light it rapidly decomposes with loss of bromine.

0.1740 g substance: 13.25 ml 0.1 N $AgNO_3$. Found %: Br 60.92. $C_5H_{11}ONBr_2$. Calculated %: Br 61.30.

Preparation of 1,2,4,6-hexanetetracarboxylic acid. For the preparation of the ester of 1,2,4,4,6-hexanepentacarboxylic acid, 3.5 g metallic sodium (0.15 mole) is dissolved in 50 ml absolute alcohol and to the solution is added 39.5 g triethyl ester of 1,1,3-propanetricarboxylic acid (0.15 mole). To the resultant sodium derivative is added, with cooling, 28.6 g (0.09 mole) diethyl ester of 3-bromo-1,2-propanedicarboxylic acid prepared by the method of Anschutz and Reuter [3] from itaconic acid. After working up in the usual manner, an oil is obtained which is fractionated under reduced pressure. The boiling point of the pentaethyl ester of 1,2,4,4,6-hexanepentacarboxylic acid is 200-201° at 3 mm. A yellowish oil. A repeated fractionation gave a yield of 22.5 g (55% of theory).

0.3642 g substance: 0.7522 g CO_2; 0.2452 g H_2O. 4.00 mg substance: 8.24 mg CO_2; 2.75 mg H_2O. Found %: C 56.32, 56.17; H 7.47, 7.64. $C_{21}H_{34}O_{10}$. Calculated %: C 56.52; H 7.62.

The ester of 1,2,4,4,6-hexanepentacarboxylic acid is saponified by prolonged (16 hours) digestion with excess of a saturated solution of potassium hydroxide in methyl alcohol. The solution, after cooling, is acidified with excess hydrochloric acid and evaporated in vacuum at 70-80°. Water is added several times to the dry residue and evaporation in vacuum repeated.

The dry residue is pulverized in a mortar and extracted with dry acetone. From the acetone solution an oil is deposited with the help of benzene and partly crystallizes on standing. After several recrystallizations from acetone-benzene mixture and then from acetic acid, crystals are obtained with m.p. 158-163°, decomposing at 200°.

3.60 mg substance; 6.01 mg CO_2; 1.70 mg H_2O. 4.99 mg substance: 8.31 mg CO_2; 2.43 mg H_2O. Found %: C 45.53, 45.42; H 5.28, 5.32. $C_{10}H_{14}O_8$. Calculated %: C 45.80; H 5.35.

The acid is readily soluble in water, acetone and alcohol, sparingly in benzene.

Synthesis of 1,3,4,6-hexanetetracarboxylic acid. Silberrad [4] synthesized this acid by the action of β-iodopropionic acid ester on the disodium derivative of the tetraethyl ester of ethane tetracarboxylic acid followed

by saponification of the condensation product. In the present investigation it was prepared by condensation of the sodium derivative of the triethyl ester of 1,1,3-propanetricarboxylic acid with diethyl α-bromoglutarate.

2.3 g metallic sodium (0.1 g-atom) is dissolved in 40 ml absolute alcohol, and to the solution is added 31.2 g of the triethyl ester of 1,1,3-propanetricarboxylic acid (0.12 mole). The solution is stirred at room temperature for an hour and addition is then made to it, with ice cooling, of 26.7 g (0.1 mole) diethyl α-bromoglutarate. After the cooled mixture had been stirred for 30 minutes, the alkalinity (to phenolphthalein) disappears and the solution is worked up as described previously. The boiling point of the pentaethyl ester of 1,3,4,4,6-hexanetetracarboxylic acid is 190° at 4 mm. Yield 11 g (24.6% of theory).

0.1214 g substance: 0.2510 g CO_2; 0.0817 g H_2O. 0.1335 g substance: 0.2759 g CO_2; 0.0899 g H_2O. Found %: C 56.46, 56.36; H 7.47, 7.48. $C_{21}H_{34}O_{10}$. Calculated %: C 56.50, H 7.62.

The ester is saponified by digestion (30 hours) with mechanical stirring with equal amounts by weight of concentrated hydrochloric acid and water. The solution is decolorized by heating with animal charcoal; after filtration it is then evaporated several times, using fresh portions of water, on the water bath. The residue crystallizes after standing for several days in a vacuum desiccator over sodium hydroxide. The dark, crystalline mass is recrystallized several times from acetone-benzene mixture. M.p. 216°.

0.1800 g substance: 0.3013 g CO_2; 0.0851 g H_2O. 0.2160 g substance: 0.3615 g CO_2; 0.1026 g H_2O. Found %: C 45.61, 45.63; H 5.25, 5.27. $C_{10}H_{14}O_8$. Calculated %: C 45.80; H 5.35.

Synthesis of 1,2,5,6-hexanetetracarboxylic acid. 3.5 g metallic sodium (0.15 mole) is dissolved in 75 ml absolute alcohol, and to the solution is added 26.9 g tetraethyl ester of 1,1,4,4-butanetetracarboxylic acid (0.075 mole) prepared by the method of Noyes and Kiriakidis [5]. The reaction mixture is heated for 15-20 minutes on the oil bath, and then addition is made of 31 g freshly distilled ethyl monochloroacetate (0.33 mole). Stirring and heating are continued up to the disappearance of the alkaline reaction (to phenolphthalein – about 15 hours), after which the reaction mixture is treated as usual. The boiling point of the hexaethyl ester of 1,2,2,5,5,6-hexanehexacarboxylic acid is 205-208° at 3 mm; the distillate crystallizes in the receiver, m.p. 52°. Yield 13.5 g (33.5% of the theoretical).

0.2230 g substance: 0.4542 g CO_2; 0.1552 g H_2O. 0.1882 g substance: 0.0742 g CO_2; 0.1272 g H_2O. Found %: C 55.56, 55.69; H 7.73, 7.71. $C_{24}H_{38}O_{12}$. Calculated %: C 55.59; H 7.34.

The ester is saponified and decarboxylated by prolonged digestion (35 hours) with equal amounts by weight of concentrated hydrochloric acid and water. After decolorization with animal charcoal the solution is evaporated on the water bath; water is added to the residue several times and evaporation to dryness is repeated. The dark, crystalline residue is recrystallized first from acetone-benzene, then from acetic acid and finally from water. M.p. 170-174°. Readily soluble in water, alcohol and acetone, sparingly in benzene and acetic acid.

3.39 mg substance: 5.63 mg CO_2; 1.79 mg H_2O. 3.70 mg substance: 6.15 mg CO_2; 1.90 mg H_2O. Found %: C 45.25, 45.33; H 5.87, 5.70. $C_{10}H_{14}O_8$. Calculated %: C 45.80; H 5.35.

Preparation and identification of hexanetetracarboxylic acid from the copolymer of butadiene and acrylonitrile. The tetramethyl ester of hexanetetracarboxylic acid, separated from the oxidized (with hydrogen peroxide) products of ozonolysis of the copolymer of butadiene and acrylonitrile [1], is saponified by digestion, with stirring, with hydrochloric acid diluted with an equal volume of water. Digestion is continued for 48-50 hours, after which period a small amount of insoluble resin still remains. The solution is decolorized by heating with animal charcoal and is evaporated on a bath. The residue begins to crystallize after standing for several days in a desiccator over sodium hydroxide. The crystal slurry, mixed with oil, is purified by several recrystallizations from acetone-benzene. M.p. 159-162°.

4.49 mg substance: 7.52 mg CO_2; 2.18 mg H_2O. Found %: C 45.63; H 5.39. $C_{10}H_{14}O_8$. Calculated %: C 45.80; H 5.35.

The melting point of the prepared acid corresponds to that of 1,2,4,6-hexanetetracarboxylic acid. A mixed sample of the acid from the copolymer and the synthetic product melts at 158-160°.

On the basis of these data we can definitely say that the structure of 1,2,4,6-hexanetetracarboxylic acid can be assigned to the acid derived from the copolymer.

SUMMARY

1. It is established that in the successive addition of two molecules of acrylonitrile in the copolymer molecule the α-carbon atom of one molecule adds on to the β-carbon atom of the other molecule.

2. 1,2,4,6-Hexanetetracarboxylic acid has been isolated from the butadiene-acrylonitrile copolymer and its structure elucidated.

3. 1,2,4,6-, 1,3,4,6- and 1,2,5,6-hexanetetracarboxylic acids have been synthesized.

4. A new method was developed for the preparation of the ethyl ester of β-bromopropionic acid via the hydrobromide of its imino ester.

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Received November 9, 1950

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TERTIARY ALCOHOLS CONTAINING THE CYCLOBUTYL RADICAL

IV. REACTION OF ISOPROPYLPHENYLCYCLOBUTYL CARBINOL WITH HYDROCHLORIC AND SULFURIC ACIDS

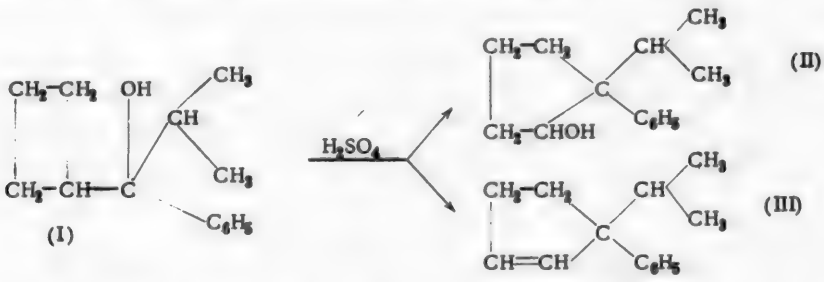
T. A. Favorskaya and I. P. Yakovlev

In previous communications [1,2,3] it was shown that when methylphenylcyclobutyl carbinol is reacted with sulfuric and hydrochloric acids it only undergoes dehydration with formation of two isomeric hydrocarbons —methylphenylmethylenecyclobutane and unsymm.phenylcyclobutylethylene. On the other hand, diisopropylcyclobutyl carbinol and ethylphenylcyclobutyl carbinol in the same conditions undergo not only dehydration but also isomerization to cyclopentane derivatives.

In this paper we consider the interaction of isopropylphenylcyclobutyl carbinol with dilute sulfuric and hydrochloric acids and also with concentrated hydrochloric acid.

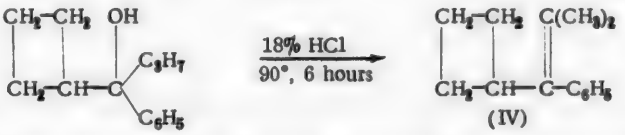
Isopropylphenylcyclobutyl carbinol (I) was synthesized from cyclobutylphenyl ketone and isopropyl magnesium bromide in 89% of the theoretical yield. A portion of the alcohol was oxidized with chromic acid mixture for investigation of its structure. Oxidation yielded isopropylphenyl ketone and a small quantity of a dicarboxylic acid with m.p. 86°. Judging by the analysis of its silver salt, this acid was α,α-isopropylphenylglutaric acid.

When heated with 25% sulfuric acid, isopropylphenylcyclobutyl carbinol isomerizes to 1,1-isopropylphenylcyclopentanol-2 (II), which was isolated in very small yield (1.6%) and had m.p. 57°, while the main bulk of the alcohol was dehydrated to 1,1-isopropylphenylcyclopentene-2 (III):

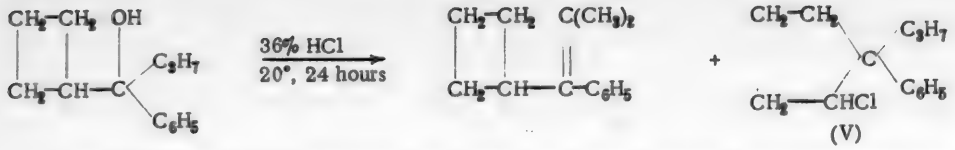


Among the products of ozonization of the unsaturated hydrocarbon (III) was found an acid with m.p. 126°; on the basis of analysis of its silver salt the formula of α,α-isopropylphenylglutaric acid can be ascribed to it. Obviously the acid was here obtained in a purer form than by the oxidation of the alcohol.

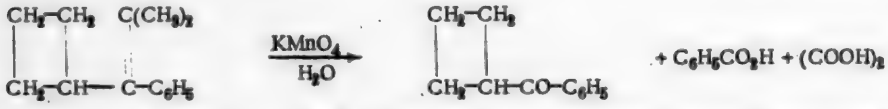
Heating with 18% hydrochloric acid for 6 hours at 30° leads to formation of 86.5% of the unsaturated hydrocarbon 1,1-dimethyl-2,2-phenylcyclobutylethylene (IV). 13.5% of the original alcohol was recovered unchanged.



With 36% hydrochloric acid, (I) gave 21% of the chloride (V) and 32% of the hydrocarbon (IV), while 47% of the alcohol was recovered unchanged. The reaction was performed at 0° for 24 hours. When the experiment was repeated at 20°, it was found that about 50% hydrocarbon and about 50% chloride (V) were formed:

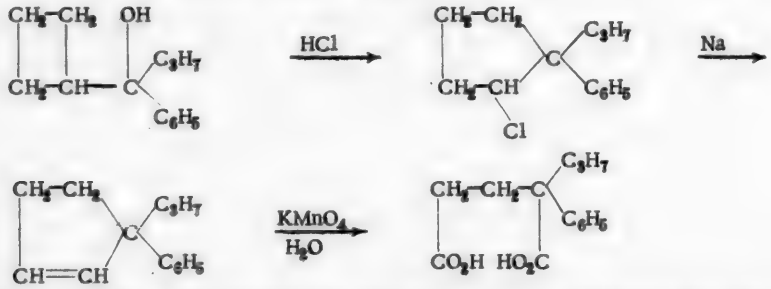


Oxidation of the unsaturated hydrocarbon (IV) with $KMnO_4$ solution proceeded very slowly and yielded cyclobutylphenyl ketone as the main product together with oxalic and benzoic acids. Acetone could not be detected. The slow oxidation of the hydrocarbon was probably due to the steric effect of the groups surrounding the double bond. The benzoic acid was formed by oxidation of cyclobutylphenyl ketone, and oxalic acid by oxidation of the succinyl residue.

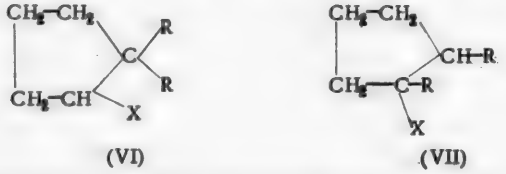


Chloride (V) had ω_{FCD} 23.6, i.e. lower than is required by a chloride containing the cyclobutyl radical (27.3). On the basis merely of the relative dispersion it can be concluded that the structure of the chloride was isomeric to that of the original alcohol. Heating of the chloride for 7-8 hours with 10% potassium carbonate and KOH solutions at the boiling temperature did not lead to reaction. It did not react in boiling absolute ether and with Mg. Heating of the chloride at 100° with sodium ethylate also gave a negative result, the chloride being recovered unchanged. Only by distillation over metallic sodium was it possible to split off HCl and to obtain an unsaturated hydrocarbon with ω_{FCD} 29.0. This behavior of the chloride indicated that it was secondary or primary but not tertiary. Oxidation of the unsaturated hydrocarbon with $KMnO_4$ solution gave a dicarboxylic acid, α,α-isopropylphenylglutaric acid, with m.p. 120-123° instead of 126° for the product of ozonization (III).

Consequently the formation of α,α-isopropylphenylglutaric acid provides confirmation that the initial hydrocarbon was 1,1-isopropylphenylcyclopentene-2, while the chloride was 1,1-isopropylphenyl-2-chlorocyclopentane. The reaction proceeded according to the scheme:



On comparing N. M. Kizhner's data [4] for isomerization with strong HBr and HI of dimethyl- and diethylcyclobutyl carbinols with our data for isomerization with hydrochloric and sulfuric acids of diisopropylcyclobutyl carbinol, we can conclude that concentrated HBr and HI act on dimethyl- and diethylcyclobutyl carbinols to bring about isomerization in the direction of expansion of the ring and formation of two isomeric halides with and without migration of the R-groups (VI) and (VII):

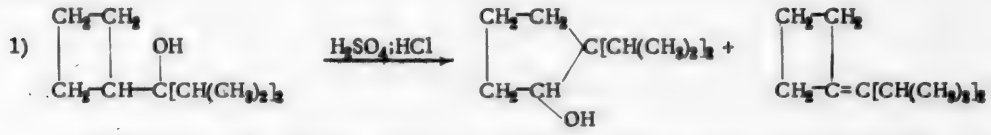


(VI) (VII)

Concentrated HCl acts on diisopropylcyclobutyl carbinol to cause isomerization with ring expansion and formation of a product of the type of (VII).

If we assign an identical isomerizing action to the halo acids, then increase in volume of R should favor the process of isomerization in the direction of derivatives of type (VI).

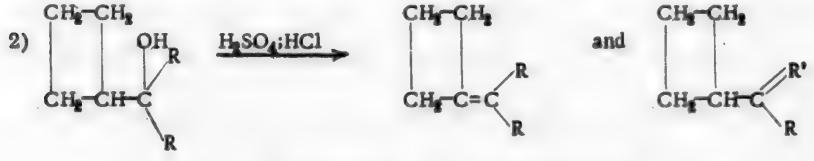
Dilute HCl and H_2SO_4 react with diisopropylcyclobutyl carbinol to form an unsaturated hydrocarbon with retention of the cyclobutane ring and to form a very small amount of an isomeric alcohol of the cyclopentane series.



Replacement of the aliphatic radical by an aromatic radical slightly changes the course of the transformation of tertiary alcohols containing the cyclobutyl radical.

Dilute hydrochloric and sulfuric acids thus act upon methylcyclobutylphenyl carbinol to cause only dehydration with formation of unsaturated hydrocarbons. No isomerization is observed.

With increasing weight of the aliphatic radical the direction of the reaction changes. Thus, ethylphenylcyclobutyl carbinol shows a greater tendency than methylphenylcyclobutyl carbinol to give unsaturated hydrocarbons without isomerization. Isopropylphenylcyclobutyl carbinol readily gives unsaturated products and chloride. In this respect there is clear evidence of the direct influence of radicals on the direction of the reaction. Whereas in the case of methyl- and ethylcyclobutyl carbinols only dehydration(and chloride formation) took place in presence of HCl and H_2SO_4 with retention of the 4-membered ring, in the case of isopropylcyclobutylphenyl carbinol only isomerization with or without dehydration of the isomerized product takes place; when using dilute hydrochloric acid dehydration takes place without isomerization.



where R = CH_3; C_2H_5; R' = CH_2; $CH{-}CH_3$.

To a certain degree the suggestion put forward in the first paper that the mechanism of the isomerizing and dehydrating action of mineral acids depends on their character is valid. As an example we may cite the dehydration of methyl-, ethyl- and isopropylcyclobutylphenyl carbinols which proceeds in various directions depending upon the acid; whereas with sulfuric acid dehydration involves the cyclobutyl radical and ring expansion, with hydrochloric acid it involves the aliphatic radical without isomerization.

EXPERIMENTAL

1. Synthesis of isopropylcyclobutylphenyl carbinol. To 12.5 g magnesium turnings moistened with 20 ml absolute ether was added dropwise 63 g isopropyl bromide dissolved in 200 ml ether, and then a solution of 80 g cyclobutylphenyl ketone in 100 ml absolute ether. The reaction was carried out without heating for 10 hours. The formed organomagnesium complex was decomposed with pieces of ice, the ether layer decanted off, and the residue acidified with dilute (1:5) hydrochloric acid and extracted with ether. The ether extract was washed with sodium carbonate solution, then combined with the ethereal solution and dried over Na_2SO_4. The ether was driven off and the residue distilled to give 92 g of an alcohol with b.p. 131-136° at 11 mm. A second fractionation yielded 91 g of alcohol with b.p. 131-133° at 11 mm; yield 89% of the theoretical. The alcohol was a weakly mobile, colorless liquid with a tarry odor and the following constants:

n_D^{20} 1.5325; ω_{FCD} 27.5; d_4^0 1.0248; d_4^{20} 1.0129; MR_D 62.5; calculated 62.0.

0.2029 g substance: 0.6120 g CO_2; 0.1715 g H_2O. 0.0348 g substance. 16.65 g benzene: Δt 0.053°. Found %: C 82.31; H 9.46; M 198. $C_{14}H_{20}O$. Calculated %: C 82.35; H 9.80; M 204.

2. Oxidation of the alcohol $C_{14}H_{20}O$. 10 g of the alcohol was oxidized with 50 g potassium bichromate, 60 g sulfuric acid (s.g. 1.84) and 200 ml water. The alcohol was added dropwise to the chromic acid mixture heated to 55°. The temperature was then raised to 68°. Oxidation required 4 hours, after which the oxidation products were extracted with ether. From the ether extract was obtained 1.1 g of a dicarboxylic acid with m.p. 86° (from water) in the form of fine white crystals (α,α-isopropylphenylglutaric acid).

0.1131 g substance: 8.6 ml 0.1 N NaOH (titer 0.003941). 0.3204 g substance: 0.1488 g Ag. Found: equiv. 133.5; % Ag 46.47. $C_{14}H_{18}O_4$. Calculated: equiv. 125. $C_{14}H_{16}O_4Ag_2$. Calculated %: Ag 46.55.

From the neutral oxidation products was isolated 3.1 g isopropylphenyl ketone. The melting point of its semicarbazone was 182°. No depression of m. pt. of the authentic semicarbazone. 4.5 g of original alcohol was recovered unchanged.

3. Reaction of isopropylcyclobutylphenylcarbinol with sulfuric acid. 15 g of the alcohol in 15 ml 25% sulfuric acid was heated for 6 hours at a temperature of 90°. The reaction product was extracted with ether, dried over $MgSO_4$ and fractionated. It was found, however, that only 1/3 of the alcohol had reacted and 2/3 was recovered unchanged. The period of contact was then doubled. The amount of unconverted alcohol was then 1/3.

After repeated fractionations and two distillations over metallic sodium, a hydrocarbon was isolated with b. pt. 235-238° at 758 mm and 103-107° at 7 mm.

n_D^{20} 1.5340; ω_{FCD} 31.5; d_4^0 0.9547; d_4^{20} 0.9357; MR_D 61.79; calculated 60.65.

0.1516 g substance: 0.5033 g CO_2; 0.1260 g H_2O. 0.0639 g substance; 16.9 g benzene: Δt 0.106°. Found %: C 90.58; H 9.30; M 182. $C_{14}H_{18}$. Calculated %: C 90.32; H 9.67; M 186.0

4.6 g of the hydrocarbon was ozonized in chloroform. After removal of the solvent, the ozonide was decomposed with water with addition of 20 ml of 10% hydrogen peroxide during digestion under a reflux condenser for 10 hours, after which the solution was made alkaline to phenolphthalein with KOH. No neutral products were obtained in the ozonolysis. From the acidic products was isolated 1.2 g of an acid with m. pt. 126°. The analytical data identify it as α,α-isopropylphenylglutaric acid.

0.1210 g substance: 9.5 ml 0.1 N NaOH (titer 0.003941). 0.3321 g substance: 0.1479 g Ag. Found %: Ag 46.18: equiv. 129.3. $C_{14}H_{16}O_4Ag$. Calculated %: Ag 46.55. $C_{14}H_{18}O_4$. Calculated: equiv. 125.0.

From the residues after distillation of the hydrocarbon was obtained 0.5 g of a crystalline alcohol with m.p. 57° in the form of long, stout prisms (from ethyl alcohol). Yield 1.6%, camphor-like odor.

0.0805 g substance: 0.2412 g CO_2; 0.0707 g H_2O. 0.0769 g substance; 16.80 g benzene: Δt 0.116°. 0.1088 g substance: 14.2 ml CH_4 (14.2°, 758.2 mm). Found %: C 81.97; H 9.82, M 198.5; active H 0.55. $C_{14}H_{20}O$. Calculated %: C 82.35; H 9.80; M 204.0; active H 0.49.

By analogy with the results obtained in the investigation of the reaction of sulfuric acid with other alcohols of the cyclobutane series, this alcohol is probably 1,1-isopropylphenylcyclopentanol-2.

4. Reaction of isopropylcyclobutylphenyl carbinol with 18% hydrochloric acid. 15 g of the alcohol and 20 ml 18% hydrochloric acid were heated for 6 hours at 90°. The reaction product was diluted with 20 ml water, extracted with ether, dried over $MgSO_4$ and distilled. The main product was an unsaturated hydrocarbon (10.1 g) with b.p. 111-115°, which was combined with the hydrocarbon obtained from the alcohol by reaction with 36% HCl; in addition 2 g of a fraction with b.p. 123.5-126°, consisting of the original alcohol contaminated with hydrocarbon.

5. Reaction of isopropylcyclobutylphenyl carbinol with 36% HCl. 15 g of the alcohol and 65 ml of 36% HCl, cooled to 0°, were brought together and left at this temperature for 24 hours. The mixture was then diluted with 200 ml iced water, and the reaction product was extracted with ether, washed with water, dried over $MgSO_4$ and distilled to give three fractions: I) 107-121° (4.2 g); II) 121-130° (7.0 g); III) 135-143° (3.2 g).

The experiment was repeated at 20°. In this case the intermediate fraction was extremely small and the amounts of fractions I and III were 6.6 g and 6.1 g.

Fraction I was an unsaturated, colorless, readily mobile hydrocarbon with a camphorlike odor; after three distillations over sodium the b.p. was 105-108° at 8 mm.

n_D^{21} 1.5355; ω_{FCD} 34.5; d_4^0 0.9643; d_4^{21} 0.9482; MR_D 61.12; calculated 60.65.

0.1245 g substance: 0.4118 g CO_2; 0.1117 g H_2O. 0.0638 g substance; 17.05 g benzene: Δt 0.104°. Found %: C 90.26; H 10.04; M 180.1. $C_{14}H_{18}$. Calculated %: C 90.32; H 9.68; M 186.0.

Fraction III: chloride, a weakly mobile liquid with a yellow tint; does not decolorize permanganate solution; b.p. 140-145° at 8 mm.

n_D^{21} 1.5422; ω_{FCD} 23.6; d_4^{21} 1.0655; MR_D 65.76; calculated 65.83.

0.2860 g substance: 0.1801 g AgCl. 0.0735 g substance; 16.90 g benzene: Δt 0.105°. Found %: Cl 15.58; M 208.1. $C_{14}H_{19}Cl$. Calculated %: Cl 15.95; M 222.5.

6. Oxidation of the hydrocarbon obtained with hydrochloric acid. Oxidation of 9.5 g hydrocarbon required 26.4 g $KMnO_4$. Oxidation proceeded very slowly (4 days). The $KMnO_4$ was introduced in small portions as the reaction proceeded. The neutral products were steam-distilled, extracted with ether and dried over $MgSO_4$. Cyclobutylphenyl ketone (5.4 g) was isolated from them. The semicarbazone of the ketone melted at 177° and did not depress the melting point of an authentic specimen. Oxalic acid with m.p. 184.5° was isolated from the acidic portion. It did not depress the melting point of an authentic specimen. In addition benzoic acid (1.3 g) was found, m.p. 120.5°, no depression in mixed melting test.

7. Hydrolysis of the chloride $C_{14}H_{19}Cl$. No reaction occurred when 6 g chloride was refluxed with 100 ml of 10% potassium carbonate solution on a heater, the chloride being recovered unchanged. Similarly no reaction took place after 6 g chloride had been digested with 56 ml 10% KOH solution for 8 hours. No reaction occurred with magnesium turnings in boiling absolute ether.

8. Cleavage of HCl from the chloride $C_{14}H_{19}Cl$. 15 g dry sodium ethylate and 10.5 g chloride were heated for 5 hours under a reflux condenser at 100°. After extraction of the reaction product it was found that the chloride was recovered unchanged. It was then distilled twice over metallic sodium. From 12 g chloride was obtained 6.5 g unsaturated hydrocarbon.

The hydrocarbon was a colorless, mobile liquid with a camphor-like odor. B.p. 240-244° at 762 mm, 111-112° at 10 mm.

n_D^{20} 1.5284; ω_{FCD} 29.0; d_4^0 0.9520; d_4^{20} 0.9385; MR_D 61.07; calculated 60.65.

0.0977 g substance: 16.80 g benzene: Δt 0.157°. Found: M 184.8. $C_{14}H_{18}$. Calculated: M 186.0.

9. Oxidation of hydrocarbon $C_{14}H_{18}$ obtained from the chloride. To 6 g hydrocarbon in 100 ml water was gradually added $KMnO_4$ with progressive consumption; oxidation consumed 14.3 g $KMnO_4$. The neutral products were distilled off in steam. The amount was 1.2 g, but a pure substance could not be isolated by distillation, nor could a semicarbazone be isolated.

From the acidic portion was isolated α,α-isopropylphenylglutaric acid (2.7 g) in the form of a pasty mass, but it could not be crystallized there and then. The neutralization equivalent of the mass was 155.0 as compared with 125.0 required for a dicarboxylic acid.

0.3913 g substance: 0.1808 g Ag. Found %: Ag 46.25. $C_{14}H_{16}O_4Ag_2$. Calculated %: Ag 46.55.

After drying for 4 months on a porcelain tile and repeated crystallization from water, a minute amount of the crystals of this acid was isolated with m.p. 120-123°. Consequently, on the basis of the analysis of the silver salts and to some extent on the basis of the melting point, we can assign to this acid, like the acid obtained from the products of ozonization of 1,1-isopropylphenylcyclopentene-2, the structure of α,α-isopropylphenylglutaric acid. The structure of the products from which it was prepared by oxidation has thus been also clarified.

SUMMARY

1. Isopropylphenylcyclobutyl carbinol has been prepared.

2. It is shown that heating of isopropylphenylcyclobutyl carbinol with 25% sulfuric acid causes isomerization to a secondary alcohol of the cyclopentane series — 1,1-isopropylphenylcyclopentanol-2, the greater part of which under these conditions dehydrates to 1,1-isopropylphenylcyclopentene-2.

3. Heating of isopropylphenylcyclobutyl carbinol with 18% hydrochloric acid results in dehydration to 1,1-dimethyl-2,2-phenylcyclobutylethylene.

4. Heating of isopropylphenylcyclobutyl carbinol with 37% hydrochloric acid results in formation of equal parts of 1,1-dimethyl-2,2-phenylcyclobutylethylene and a chloride, a derivative of cyclopentane.

5. Distillation of the chloride over metallic sodium results in cleavage of hydrogen chloride with formation of the hydrocarbon 1,1-isopropylphenylcyclopentene-2.

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Received December 14, 1950

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* See Consultants Bureau translation, p. 133.
** See Consultants Bureau translation, p. 143.
*** See Consultants Bureau translation, p. 267.

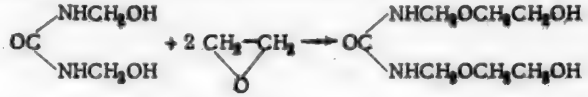
THE REACTION OF DIMETHYLOLUREA WITH ETHYLENE OXIDE

K. D. Petrov and O. K. Gosteva

The reaction of ethylene oxide with urea (as well as with other amides) was described in 1930 by Dreyfus [1] in a patent on the preparation of monoalkanolamines. In accordance with the specification the urea was added to the ethylene oxide in aqueous solutions. The prepared products were not investigated and were subjected to hydrolysis in presence of alkali with the aim of obtaining monoethanolamine.

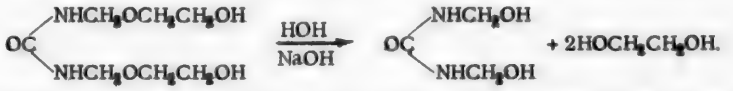
Later, Paquin [2] applied this reaction to the preparation of diethanolurea by passing gaseous ethylene oxide into a saturated aqueous solution of urea heated to 90-95°. The investigator noted that in these conditions the diethanolurea undergoes further transformations to give resins which have technical importance.

Up to the present the reaction of the most important urea derivative – dimethylolurea – with ethylene oxide has not been investigated. Dimethylolurea is known to contain, apart from the labile hydrogen atoms linked to nitrogen, extremely labile methylol groups. Consequently it resinifies readily. Resinification proceeds under the action of heat and various chemical agents, particularly acids. In our opinion ethylene oxide need not cause undesirable transformations of dimethylolurea. Thus, when heated for a long period with ethylene oxide at 100° in a sealed tube, dimethylolurea does not exhibit signs of change. In the presence, however, of dimethylaniline (which itself does not provoke visible changes in dimethylolurea), dimethylolurea entered into reaction with ethylene oxide to form a viscous, colorless oil. We took dimethylolurea and ethylene oxide in ratios of 1:2 to 1:3, and concordant results were obtained in all cases. Analysis of the oil for content of hydroxyl groups, and nitrogen and other investigations showed that the product is a dihydric alcohol [3]. The structure of the latter requires elucidation. It is known that urea in aqueous solution reacts with ethylene oxide to form diethanolurea; the question therefore arose whether in our case also the dimethylolurea added on to ethylene oxide at the amide group. To test this point, we heated urea with ethylene oxide in presence of dimethylaniline in a sealed tube in the same conditions as for dimethylolurea; no reaction between urea and ethylene oxide was here observed. We may therefore conclude that addition of dimethylolurea to ethylene oxide proceeds not at the amide group but at the hydroxyl group according to the scheme:



(1)

Evidence for this reaction course is obtained by hydrolysis of the product in presence of sodium hydroxide when ethylene glycol is formed. The latter could only result from cleavage of the bis-β-hydroxyethyl ether of dimethylolurea (I). The hydrolysis of (I) is a rather complex process, but the following reaction (leading to ethylene glycol) could take place in addition to other reactions:



The foregoing considerations support the structure (I) for our product and demonstrate the mode of addition of dimethylolurea to ethylene oxide.

It should be noted in conclusion that if addition of dimethylolurea to ethylene oxide had taken place at the amide group with formation of dimethyloldiethanolurea, then hydrolysis should yield ethanolamine, whereas the latter was not found.

EXPERIMENTAL

Preparation of bis-β-hydroxyethyl ether of dimethylolurea. The starting material was dimethylolurea with m.p. 129°. We give details of one of the numerous experiments.

Into a stainless steel tube were introduced 50 g (0.416 mole) dimethylolurea, 55 g (1.25 mole) ethylene oxide, a few drops (3-4 drops) dimethylaniline and 50 ml benzene. The tube was hermetically sealed and attached to the rotating shaft of a water bath whose temperature was maintained at 95-100°. The reaction proceeded for 2-1/2 hours. At the conclusion of the reaction the product was extracted from the tube, cooled, separated from the benzene layer and further heated in vacuum on the water bath for removal of traces of benzene and other volatile impurities.

Distillation was effected at first in a low vacuum and later at 3-4 mm, the bath temperature being brought to 130°. The yield of bis-β-hydroxyethyl ether of dimethylolurea was quantitative.

To the naked eye the substance is a viscous, transparent, yellow oil: n_D^{22} 1.5044. When prepared in a glass ampoule, however, the product is colorless.

d_{20}^{21} 1.2830; n_D^{21} 1.5010; MR_D 47.53; calculated 45.58.

0.3682 g substance: 0.5586 g CO_2; 0.2706 g H_2O. 0.4839 g substance: 0.7345 g CO_2; 0 3602 g H_2O. Kjeldahl nitrogen determination: 1.0720 g substance: 9.83 ml 1 N H_2SO_4. Determination of hydroxyl groups by phthalation: 0 5031 g substance: 9.62 ml 0.5 N KOH. 0.2230 g substance: 4.19 ml 0.5 N KOH. 0.4938 g substance: 37.03 g water; Δt 0.120°. Found %: C 41.39, 41.42; H 8.22, 8.36; N 12.84; OH 16.25, 15.98; M 206. $C_7H_{16}O_5N_2$. Calculated %: C 40.34; H 7.69; N 13.46; OH 16.35; M 208.

Hydrolysis of bis-β-hydroxyethyl ether of dimethylolurea. Into a round-bottomed flask, fitted with stirrer and reflux condenser, were introduced 104 g (0.5 mole) bis-β-hydroxyethyl ether of dimethylolurea and 100 ml 1 N sodium hydroxide. The contents of the flask were heated on an oil bath to the boiling point of the reaction mixture. Hydrolysis was carried out for 20 hours.

At the conclusion of hydrolysis, the reaction mass was cooled and transferred to a Claisen flask for removal of water by distillation on the water bath while connected to a water jet pump. The distillate had an ammoniacal odor. After the water had been distilled off, the reaction product was extracted with 300 ml butanol. The butanol was subsequently distilled off in a low vacuum; the residue was filtered and subjected to fractionation. The main fraction came over at 104-106° (12-15 mm). The product weighed 12 g and was a transparent liquid. It contained 47.20% OH and traces of nitrogen: d_{20}^{20} 1.1126; n_D^{20} 1.4401.

Fractionation of the liquid at normal pressure gave the following results: I, up to 194°, 0.5 g, n_D^{20} 1.4300; II, 194-198°, 6 g, n_D^{20} 1.4324 d_{20}^{20} 1.1126; III, 198-200°, 2 g, n_D^{20} 1.437 0; IV, 200-205°, 1 g; still residue 2.5 g.

The substance coming over at 194-198° corresponded to ethylene glycol in specific gravity, boiling point and refractive index; the literature constants of ethylene glycol are [4]: b.p. 197.5°, d_{20}^{20} 1.1151; n_D^{20} 1.4335. We did not investigate further the crystalline nitrogen-containing compounds isolated from the alkaline hydrolyzate.

SUMMARY

The reaction between dimethylolurea and ethylene oxide is described and the mode of addition of dimethylolurea to ethylene oxide is clarified.

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Received May 15, 1951

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NEW TYPES OF TERPENE TRANSFORMATIONS

XL THE ACTION OF CHLORINE ON α-FENCHENE

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Derivatives of fenchenes with the composition $C_{10}H_{17}X$ are almost unknown. The action of chlorine on fenchenes has not been investigated. Since monochlorterpenes of the allylic type obtained by us for the first time can be transformed into diverse terpene derivatives of the general composition $C_{10}H_{17}X$ (see previous communications), it is a matter of some interest to investigate the action of chlorine on fenchenes and the further transformations of the chlorfenchenes.

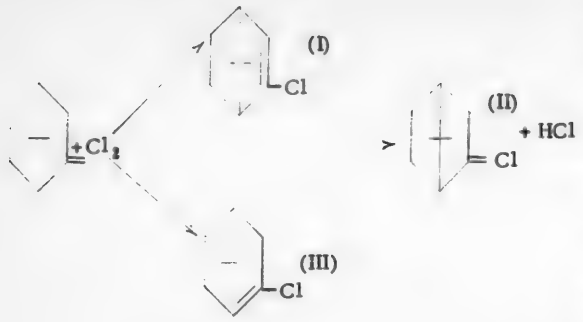
As we know, fenchenes are not found in nature and are prepared by removing water from fenchyl alcohol; this process always gives a mixture of fenchenes in which one isomer or the other predominates according to the method of dehydration. Consequently the preparation of fenchenes necessitates the use of one fenchyl alcohol or another.

Lyubomilov, Rutovsky and Sheremeteva [1] report that the liquid chloride which is a by-product of the action of hydrogen chloride on pinene can be converted under the action of potassium phenolate into a hydrocarbon $C_{10}H_{16}$. The latter can give, by the Bertram-Walbaum method, the acetate of isofenchyl alcohol. Unfortunately the authors did not state the yield of this ester. We repeated this work and found that the top terpene fractions (up to 160°), obtained from the chloride which did not solidify at −14° and which corresponded in boiling point to a mixture of fenchenes, solidified partially at only −23° and completely at −70°; this indicated the high content of camphene therein and in turn the high content of bornyl chloride in the liquid chlorides. We then froze out a solid fraction at −54° (it, too, proved to be bornyl chloride) and worked up the liquid portion by the method of Rutovsky and co-workers. In this case also, the fraction up to 160° partly solidified at −23°. It became clear from the foregoing remarks that these liquid chlorides do not constitute the raw material for an acceptable synthesis of the fenchene isomers.

It is known [2] that fennel oil has a fenchone content of 0 to 15-18% depending mainly on the place of cultivation of the fennel. The main constituent of this oil is anethole. At some perfumery factories fennel oil is oxidized with chromic acid mixture to convert the anethole into anisaldehyde, and the aldehydes are extracted from the product of reaction with bisulfite solution. Since fenchone is extremely stable to the action of oxidizing agents, it might be thought that the portion of the reaction product not soluble in bisulfite would be enriched in fenchone; this was found to be the case by experiment. By this very simple method (see experimental) we obtained pure fenchone in a yield of about 30% from this waste product of the anisaldehyde industry. In this way we solved the problem of finding a starting material for the synthesis of fenchenes.

The first stage in the synthesis is the reduction of d-fenchone to l-fenchyl alcohol (mixture of the α- and β-isomers). After trying out a number of methods we decided that the simplest, most convenient and safest method was reduction with isopropyl alcohol in presence of aluminum isopropylate [3]. In this way we obtained l-fenchyl alcohol in nearly quantitative yield. Dehydration of fenchyl alcohol gives a mixture of fenchenes. The Qvist method [4] (heating of the alcohol with aluminum phosphate) gives a mixture containing over 50% α-fenchenes. We also tried this method and fractionated the resultant mixture of fenchenes in a column with an efficiency of about 40 theoretical plates. The fenchene isomers were isolated in the pure form. The α-fenchene yield from the mixture was 59%; its specific rotation (−38.2°) was higher than that of any other sample of α-fenchene described in the literature; we therefore considered that our α-fenchene was of adequate purity.

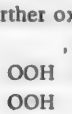
Reaction of α-fenchene with chlorine was effected in the previously described conditions [5] with cooling of the reaction mixture to −2° and −6°. In line with the previously developed considerations [6] the action of chlorine on α-fenchene may be represented by the following scheme (the saturated dichloride is not shown):

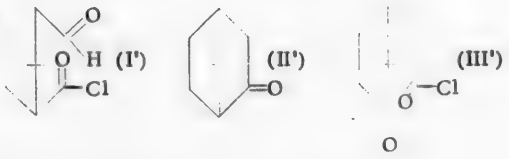


The yield of monochlorides determined from the amount of hydrogen chloride ("anomalous" reaction) fluctuated round 63%, which is not remarkable: we had previously shown [7] that the highest yield from this reaction must occur when the positive end of the double bond is attached to one or two methyl groups with their more highly protonized hydrogens. In the present case the double bond has attached to it a methylene and a methiene group. Consequently the most probable course of reaction (I) will not be realized with a sufficiently high yield (due to the "methylene" prohibition), as we have already observed in the case of β-pinene [5]. Formation of chloride (III) is very much less probable (Bredt prohibition). Formation of chloride (II) is analogous to the formation of 1-chlor-2,2'-diphenylethylene by the action of chlorine on 2,2'-diphenylethylene: in the latter case the removal of a hydrogen atom from the phenyl group with the labile double bond is impossible, and the chlorine anion captures the hydrogen from the methylene group which is protonized by the action of the chlorine cation undergoing attachment. In our case the migration of the double bond with formation of chloride (I) is not excluded but is hindered ("methylene" prohibition), and hence chloride (II) must be formed in small yields. Previously we discussed [6] the predominance of this course of chlorination in the case of the extremely "prohibited" molecule of camphene.

The α-fenchyl monochloride isolated from the chlorination products has a sharp boiling point, which points to the absence of chlorides with different positions (primary, secondary and tertiary) of the atoms of chlorine. On the other hand it exhibits appreciable exaltation of the molecular refraction (+0.3) which is not consistent with the presence solely of chloride (I) and points to contamination with chloride (II) with a hemicyclic double bond. The contents of total and saponifiable chlorine (20.6 and 16.2 %) also point to the same conclusion: it contains three parts chloride with labile double bond [possibly (I)] and one part of an unsaponifiable chloride [possibly (II)]. Further investigations confirmed the correctness of these suppositions.

Ozonolysis of the mixture of chlorides should give from chloride (I) a chlorketone with the composition $C_{10}H_{15}O_2Cl$ (I'), from chloride (II) a fenchocamphorone with the composition $C_9H_{14}O$ (II'), and from chloride (III) a chlordiketone with the composition $C_{10}H_{15}O_2Cl$ (III').

On further oxidation only (I') will give cis-apocamphoric acid  , (II') is stable to oxidation, (III') will not give the acid.



Actually, ozonolysis only gives the chlorketoaldehyde (I') which is oxidized to cis-apocamphoric acid. Fenchocamphorone could not be isolated after ozonolysis of the mixture of chlorides. Chloride (II) was detected in the mixture after conversion of chloride (I) into the acetate of fenchenol which has a higher boiling point than chloride (II) (the latter does not react with potassium acetate) Ozonolysis of the isolated chloride (II) gave fenchocamphorone which was characterized in the form of the semicarbazone.

Chloride (I) is a derivative of γ-fenchene. Substitution of its chlorine by the hydroxyl group will give the unknown γ-fenchenol if this transformation is not accompanied by an allyl rearrangement, and it will give the unknown α-fenchenol if an allyl rearrangement ensues. As was pointed out in the preceding communications, the thermodynamic probability of such a rearrangement is extremely low. Transformation of the chloride into the alcohol was effected by the usual method via the acetate by heating (I) with potassium acetate in boiling acetic acid. The ester is obtained in good yield; its molecular refraction is normal, pointing to the absence of the ester of α-fenchenol with a hemicyclic double bond. The derived γ-fenchenol yielded an acid phthalate when heated with phthalic anhydride in boiling benzene, demonstrating the primary character of the alcohol. The same alcohol was oxidized by chromic acid in acetic acid to the corresponding aldehyde. Consequently our prepared alcohol can be taken to be γ-fenchenol, corresponding to chloride (I) in structure. It is

the first representative of the alcohols of the γ-fenchene series.

EXPERIMENTAL

1. Check of the possibility of preparing fenchyl alcohol from the liquid monochlorides of composition $C_{10}H_{17}Cl$, forming a by-product of the preparation of bornyl chloride from pinene. Technical monochloride (1338 g) was fractionated in a column to give 242 g terpenes. The residue was frozen at −14° and 362 g crystals (bornyl chloride) were drained off; the filtrate was fractionated in a plate column to give eight fractions. The first six fractions solidified at +20°; these were drained at the pump and the filtrate again frozen at −14° to give 554 g of crystals (41% of the batch weight) and 242 g of chlorides with composition $C_{10}H_{17}Cl$ liquid at −14° (18%). A portion of the liquid chlorides was converted into terpenes by Rutovsky's method [1]. The 150-160° fraction (all the fenchenes boil below 160°) solidified at −23°; consequently it mainly consists of camphene. The original liquid chloride was then frozen at −54° and the crystals (bornyl chloride, 60%) drained at the pump. The chlorides remaining liquid at −54° were about 70% technical monochloride; they were again converted into terpenes which boiled at 155-175°. The fraction up to 160° was again frozen at −23° but not completely. It was concluded that this method could not give fenchenes in satisfactory yield.

2. Preparation of fenchone. The sodium bisulfite-insoluble portion of the products of oxidation of fennel oil with sulfuric acid solution of bichromate (8967 g) was steam-distilled. Distillation was stopped when 5 ml oil per 100 ml water came over. The amount of distilled oil was 5397 g (60%); the residue was 3402 g (38%). The oil was fractionated in a column with 6-8 theoretical plates and at a pressure of 10-11 mm. Fractions corresponding to fenchone in boiling point were combined and again fractionated in the same conditions. 307 g of fractions was obtained with boiling point at atmospheric pressure of 185-191.5° (10.4% yield on the volatile oil); 1347 g (46%) was obtained with boiling point 191-193.5° (the boiling point was determined by distilling 10 g from a small Wurtz flask which accounts for the wide range; in vacuum, on a column, the fraction boiled sharply). Its constants were: d_4^{20} 0.9408; n_D^{20} 1.4623; $[\alpha]_D^{20}$ + 78.3°. The oxime was prepared by Wallach's method [8]; the melting point of the first precipitate was 164-166°; that of the second precipitate, after dilution of the mother liquor with a little water, was 164-165°. 10 g of fraction gave 8.9 g oxime. The main 185-191.5° fraction was purified by digestion with triple the volume of nitric acid (density 1.41) until nitrogen oxides ceased to come off. Fenchone was obtained from it (by dilution with water, steam-distillation and fractionation) in a yield of 55% of the top fraction. Its constants were: b.p. 191-192.5°; d_4^{20} 0.9429; n_D^{20} 1.4624; m.p. of oxime 165-166°.

3. Reduction of fenchone. Into a round-bottomed flask, heated to 45-50° and fitted with a reflux condenser, are introduced a weighed amount of aluminum turnings, absolute isopropyl alcohol in weight equivalent to one-eleventh of the weight of the aluminum turnings, and mercuric chloride in amount equivalent to 5% of the weight of the aluminum turnings. After solution of the aluminium, the flask is connected to a column with 7-8 theoretical plates and addition is made to the flask of fenchone in amount equivalent to ten times the weight of the turnings, dissolved in three times the volume of isopropyl alcohol. The flask is heated on the boiling water bath and the acetone formed is taken off with a reflux number of 25-30 (vapor temperature 58-65°). After 40 hours addition is made of isopropyl alcohol in amount equal to 1-1½ times the amount of fenchone and heating is continued for a further 40 hours. About 65% of the theoretical amount of acetone collects in the distillate (determined by the oxime method). The reaction product is agitated with double the volume of water, the aluminium hydroxide precipitate is dissolved in the calculated amount of aqueous hydrochloric acid, and the aqueous layer is separated from the oil layer. The isopropyl alcohol-water azeotrope is distilled off from the aqueous layer on a column; the oily layer is first fractionated at atmospheric pressure to remove isopropyl alcohol and then in vacuum with a reflux number of 10-12. After taking off the fenchone intended for fresh reduction, the tap of the receiver and the dephlegmator of the column become choked with crystals of fenchyl alcohol if the temperature of the water in the dephlegmator is not higher than 10°. The column is then replaced by a small tray still and the fenchyl alcohol distilled off. If the water temperature exceeds 10°, then the fenchyl alcohol fraction is taken off at the boiling temperature at atmospheric pressure (199-201°), and with a specific rotation of −10°, −14°. The fraction intermediate between fenchone and the alcohol is redistilled. The yield of the alcohol, allowing for the recovered fenchone, is nearly quantitative.

4. Dehydration of fenchyl alcohol. 47 g fenchyl alcohol and 13 g $AlPO_4$ are heated on a metal bath (bath temperature 210-220°) until oil-water mixture ceases to come off; the residue of oil in the catalyst is then removed by blowing with steam. 40.4 g oil was obtained. In this manner 536 g alcohol was worked up

to give 460 g oil. This was fractionated in a column equivalent to 40-45 theoretical plates at a pressure of 9 mm and a reflux number of 15-16. There was obtained a top fraction of 32 g (b.p. 139-142° at atm. pressure), a middle fraction of 227.4 g, and a residue of 153 g; the loss was 45 g. The residue was put aside for fresh dehydration and the middle fraction was refractionated in the specified conditions for isolation of fractions with constant boiling points; this involved three rectifications. The constants of the fractions are given in the table. The boiling points of the fractions at atmospheric pressure were determined by fractionation of small samples from a Wurtz flask and are therefore not sharp.

B.p. (760 mm)	Weight (g)	d_4^{20}	n_D^{20}	MR_D Calculated	MR_D Found	ΣMR_D
147-148°	35.3	0.8616	1.4613	43.511 γ-fenchene	43.41	−0.1
151-153	20.7	0.8663	1.47105	43.911 β-fenchene	43.933	+0.022
155-156	102.6	0.8699	1.4734	43.911 α-fenchene	43.931	+0.02

Comparison of the constants of our specimen of α-fenchene ($[\alpha]_D$ −38.2°) with those obtained by other authors [9] shows that our specimen is superior both in specific rotation and in refraction.

5. Chlorination of α-fenchene was performed under the usual conditions (with cooling to −2° to −6°): α-Fenchene 50 g, $KMnO_4$ 12.5 g, HCl 70 ml, $NaHCO_3$ 30 g, duration of chlorination 2 hours 45 minutes.

The amount of Cl' found in the salts was 4.1 g, that in the wash bottles was 0.4 g; the organic portion contained 9.7 g chlorine; the percentage of anomalous reaction was 63.4. The organic portion amounted to 55.4 g of which 51.9 g was fractionated in a small column. After distilling off the α-fenchene (21 g) a monochloride fraction (18.7 g) was collected with specific gravity 1.012; the residue of 7.5 g had specific gravity 1.112; the loss was 4.8 g.

The monochloride was fractionated in the same column at 2.3 mm to give: First fraction (following a few drops at 41-53°) at 53-55°, 5-7 g, d_4^{20} 1.000; n_D^{20} 1.4895; second fraction at 55°, 10.4 g; residue 0.7 g; loss 0.4 g.

d_4^{20} 1.018; n_D^{20} 1.4931; MR_D 48.71; calculated 48.38.

Found %: Total Cl 20.6; allyl Cl 16.2, 15.9. $C_{10}H_{15}Cl$. Calculated %: Total Cl 20.7.

9.5 g of the second fraction in 100 ml chloroform was ozonized (under ice cooling) with 55 l 4.1% ozone until the reaction to bromine was negative. The chloroform solution of the ozonide was decomposed by stirring with 200 ml iced water for 6 hours. The chloroform layer was separated, and the chloroform distilled off to leave a residue of 11.45 g; the latter was fractionated in vacuum (0.001 mm). The main fraction (3.6 g) came over at a bath temperature of 160-180°.

d_4^{20} 1.164; n_D^{20} 1.4997; MR_D 51.18. $C_{10}H_{15}ClO_2$ (chlorketoaldehyde); calculated 51.07.
Found %: C 58.2, 57.9; N 7.4, 7.3; Cl 19.9. $C_{10}H_{15}ClO_2$. Calculated %: C 59.2; H 7.4; Cl 17.5.

Oxidation of the chlorketoaldehyde. To 3.8 g of aldehyde in 100 ml acetone and 10 ml water was added a 4% permanganate solution in acetone until the color remained unchanged (195 ml) while heating to 40° on a bath. The manganese dioxide was drained at the pump and extracted three times with boiling water. The combined filtrates were concentrated to 30 ml, acidified with hydrochloric acid (to congo) and repeatedly extracted with ether. The ether was removed from the extract, the solid residue was recrystallized from hot aqueous alcohol: Needles in star-like clusters, m.p. 204-206°; g-equivalent 93.2, corresponding to cis-apocamphoric acid [10].

6. Action of potassium acetate on α-fenchyl chloride. Chloride 24.4 g, potassium acetate 38 g and acetic acid 110 ml were digested for 3 hours. The solution was diluted with water to 1 liter and extracted with ether; in the aqueous layer was found 7.2 g KCl, yield 68 %. From the ether extract, following neutralization of the acid with caustic alkali, the ether was driven off and the residue was fractionated in vacuum to give two main fractions: I) 57-59° (1.5 mm), 5.7 g; d_4^{20} 1.000; n_D^{20} 1.4793 (monochloride, see below); II) 74-75° (3 mm), 14.6 g.

d_4^{20} 0.996; n_D^{20} 1.4711; MR_D 54.46. $C_{10}H_{15}OCOCH_3$; calculated 54.40.

13.5 g of fenchyl acetate was saponified by digestion for 6 hours with 5 g potassium hydroxide in 40 ml ethanol. The ethanol was distilled off on the water bath, the residue diluted with water and extracted with ether, and the ether extract fractionated to give one main fraction; 74° at 3 mm, 6.9 g.

d_4^{20} 0.9876, n_D^{20} 1.4935; MR_D 44.8. $C_{10}H_{15}OH$; calculated 45.0.

It was qualitatively established that fenchenol in boiling benzene reacts with phthalic anhydride to form the acid phthalate, melting at about 140°. A mixture of equal amounts (1 g each) of fenchenol and the anhydride was then heated at 130° for 10 minutes, the melt extracted with sodium carbonate solution, the solution acidified, and the precipitate twice recrystallized from gasoline; fluffy needles, m.p. 144°; gram-equivalent found 299, calculated for $C_{18}H_{19}CO_2COOH$ 300.

5 g fenchenol was oxidized, under cooling, with 2.2 g chromic acid in 25 ml acetic acid. The solution was diluted with water and blown with steam; the oil from the distillate was extracted with ether, the ether driven off, and the residue fractionated at 3 mm. A fraction was collected whose constants corresponded to terpenol: b.p. 61-63°; d_4^{20} 0.952; n_D^{20} 1.4808. It gave all the qualitative reactions for an aldehyde. The semicarbazone, prepared in the usual manner, had m.p. 102-104° (from methanol).

7. Determination of the structure of the α-fenchyl monochloride not reacting with potassium acetate. 1.8 g monochloride in 50 ml chloroform was ozonized with 12 liters of 4 % ozone until the reaction for bromine was negative. The ozonide solution was decomposed by stirring for 6 hours with iced water; the chloroform layer was separated, the chloroform distilled off, and the residue distilled with steam.

The distillate was extracted with ether, the ether was removed from the extract; the residue partly solidified. To 1 g of residue was added a solution of 2 g semicarbazide acetate in 50 ml alcohol. After 24 hours the solution was concentrated to 10 ml; the precipitated crystals were recrystallized from hot alcohol until the m.p. was constant at 210-212°, which corresponds to the semicarbazide of fenchocamphorone [11].

Found%: N 22.1 (Dumas). $C_{10}H_{17}ON_3$. Calculated %: N 21.5.

SUMMARY

1. It is shown that Rutovsky's method is unsuitable for the synthesis of fenchyl alcohol.

2. A simple method was developed for the preparation of fenchone from available raw material and for the reduction of fenchone to fenchyl alcohol.

3. Fenchyl alcohol was converted into extremely pure α-fenchene in good yield.

4. Chlorine acts on α-fenchene to give γ-fenchyl chloride and ω-chlor-α-fenchene. The first of these was converted into the corresponding γ-fenchenol.

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Received April 17, 1951

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NEW TYPES OF TERPENE TRANSFORMATIONS

XII. SYNTHESIS OF NITRILES OF THE HOMOTERPENE SERIES

D. Tishchenko, N. Persiantseva and V. Foliadov

Certain nitriles of the terpene series with the composition C_9H_{15}—CN are known and can be prepared by dehydration of the oximes of the corresponding aldehydes; by contrast, the homoterpene nitriles with the composition $C_{10}H_{15}$—CN are practially unavailable. Development of a general method for their synthesis is desirable if only because, by means of a series of known transformation, we can pass from them to the almost unknown homoterpene derivatives such as the aldehydes, acids, ketones, amines and imines.

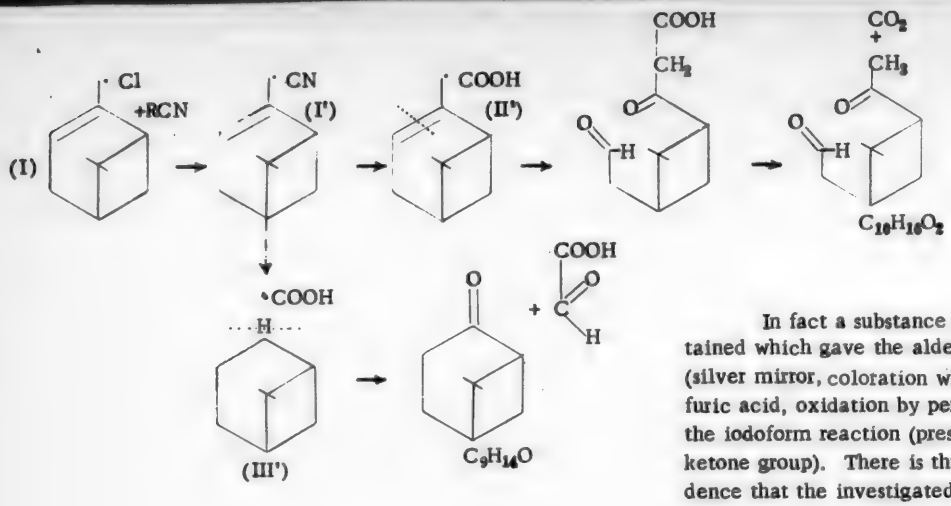
The chlorterpenes of the allyl type prepared by us contain a labile chlorine atom capable of anion exchange reactions. In communication VII [1] we put forward certain considerations enabling the establishment of the most favorable conditions for transformation of our chlorterpenes into other terpene derivatives with the help of anionic exchange. The most important of these is the presence in the reaction medium of only that anion which is necessary for formation of the desired substance. This was experimentally demonstrated by reaction of myrtenyl chloride with potassium acetate in ethanol, which gives not only myrtenyl acetate but also ethyl myrtenyl ether due to addition of the ethoxyl ion to the myrtenyl cation.

In the saturated series the synthesis of nitriles is effected with satisfactory yields by reacting halohydrins with an aqueous or alcoholic solution of alkali cyanides. On the basis of the foregoing considerations it can be predicted that this method is unacceptable for the present case. Alkali cyanides are strongly solvolyzed by ionogenic solvents and the solution will contain a high concentration of hydroxyl or alkoxyl ion which leads to formation of either alcohols or alkyl terpenic ethers. An experimental test confirmed this prediction: On reacting myrtenyl chloride with an ethanol solution of potassium cyanide, ethyl myrtenyl ether was obtained in nearly quantitative yield together with only traces of nitrile.

At high temperatures certain chlorterpenes break down with appreciable speed to dehydroterpene $C_{10}H_{14}$ and hydrogen chloride. In connection with the preparation of nitriles, therefore, we must seek cyanides which do not react, or only react with difficulty, with hydrogen chloride in order to avoid the release of hydrocyanic acid during the transformation. After several exploratory experiments we decided to make use of cuprous cyanide in a medium of boiling aromatic hydrocarbons for the synthesis of terpene nitriles. The reaction was found to proceed with extraordinary slowness in boiling benzene (check by determination of amount of inorganic chlorine), rather more quickly in boiling toluene, and with adequate speed in boiling xylene. Hardly any hydrocyanic acid was evolved, indiating that the reaction proceeds in the desired direction.

Myrtenyl chloride (I) and the chloride of carveol (6-chlordipentene, II) were consequently brought into reaction with cuprous cyanide. The nitrile of homomyrtenic acid was obtained from (I) in about 50 % of the theoretical yield, the nitrile of dipentenylformic acid was obtained from the chloride (II) in about 30% yield. Both are fairly mobile liquids with a characteristic nitrile odor, specific gravity about 0.95-0.96 and refractive index about 1.50. Both nitriles were saponified to the corresponding acids. Acid saponification is excluded in the present case, particularly for myrtenyl cyanide (I'), due to the possibility of fusion of the four-membered ring. Saponification was therefore performed with alcoholic caustic alkali. The corresponding terpenyl formic acids were obtained in good yields. We know that aqueous alkali can cause migration of the double bond in unsaturated acids [2], and it was consequently necessary to check, by one example at least, whether such a migration takes place during saponification of our nitriles.

On the basis of this method of preparation the structure (I') must be assigned to myrtenyl chloride and (II') to the acid derived from it. If double fond migration had occurred during saponification of the nitrile, the structure (III') must be assigned to the acid. Ozonolysis of acids (II') and (III') will give different products: Acid (II') will give an α-ketoaldehyde acid which in turn will give a ketoaldehyde $C_{10}H_{16}O_2$ and carbon dioxide; acid (III') will give nopinone $C_9H_{14}O$ and carbon dioxide:



In fact a substance $C_{10}H_{16}O_2$ was obtained which gave the aldehyde reactions (silver mirror, coloration with fuchsine sulfuric acid, oxidation by permanganate) and the iodoform reaction (presence of methyl ketone group). There is thus adequate evidence that the investigated acid has the structure (II') corresponding to the structure of the original chloride.

EXPERIMENTAL

(Transformations of chloride I were performed by N. Persiantseva, those of chloride II by V. Foliadov.)

Chloride (I). Small weighed amounts of the chloride were heated for various periods with excess of cuprous cyanide in boiling benzene, toluene, xylene, and the reaction yield determined from the amount of inorganic chlorine. With benzene the yield did not exceed a few per cent; with toluene it was 8% after 2 hours and 26% after 6 hours; with xylene it was 63% after 3 hours.

100 g chloride, 50 g cuprous cyanide and 500 g xylene were heated for 5 hours at the boil, after which the copper salts were filtered at the pump, the low-boiling substances (xylene, etc.) were distilled off on the boiling water bath in the vacuum of a water jet pump, and the residue fractionated in a small column at a pressure of 3 mm. One main fraction (38 g) was obtained with b.pt. 99-102°.

d_4^{20} 0.961; n_D^{20} 1.4889; MR_D 48.34. $C_{10}H_{15}CN$. Calculated 48.30.

Found %: N 8.53, $C_{11}H_{15}N$. Calculated %: N 8.69.

Saponification of the nitrile. 15 g nitrile was heated with 12 g potassium hydroxide in 100 ml 85% alcohol until no more ammonia came off (76 hours). After the alcohol had been distilled off, the neutral substances were extracted from the solution with ether and the alkaline solution was acidified with hydrochloric acid (to congo) and extracted with ether. The ether was removed from the ether extract and the residue fractionated in a small column at a pressure of $1 \cdot 10^{-3}$ mm. A main fraction was obtained (10.5 g) with b.p. 110-112°. A viscous liquid:

d_4^{20} 1.048; n_D^{20} 1.4977; MR_D 50.29. $C_{10}H_{15}COOH$. Calculated: 50.07.

Found %: C 73.0, 73.3; H 8.8, 8.8; equiv. 179.7, 178.7. $C_{10}H_{15}COOH$. Calculated %: C 73.3; H 8.9; equiv. 180.

Ozonization of the acid. 7 g acid in 100 ml chloroform was treated with 58 liters 4% ozone for removal of the reactivity to bromine. The chloroform solution of the ozonide was added dropwise to iced water with stirring, 1 g manganese dioxide was added and the stirring continued until the reaction for peroxide was negative. The manganese dioxide was drained off at the pump and the chloroform layer fractionated. The main fraction came over at 45° (0.000001 mm) and gave all the aldehyde reactions and the iodoform test.

Found %: C 70.1, 69.9; H 9.7, 9.9. $C_{10}H_{16}O_2$. Calculated %: C 71.4; H 9.5.

Chloride (II). 49 g 6-chlordipentene, 32 g cuprous cyanide and 300 ml xylene were heated for 3 hours at the boil, after which the copper salts were filtered at the pump, washed with xylene and dried. The dry salts were fused with a mixture of 32 g Na_2CO_3 and 64 g $KHCO_3$ (inflammable vapor came off in large volume during fusion) and the melt was dissolved in water, the solution filtered from the precipitate and made acid to phenolphthalein in a draft at the boil. In the solution was found 8.55 g chlorine ion; the reaction had proceeded to the extent of 85%. The xylene was distilled off from the xylene solution in a column at 20 mm to leave 36.2 g

residue which was then fractionated at 1 mm. Up to 95°, 0;5 g; fraction I) 98-99°, 5.8 g; fraction II) 99-103°, 4.2 g; undistillable viscous residue 14.2 g (nitrogen content 4%).

Fraction I: d_4^{20} 0.9577; n_D^{20} 1.5001; MR_D 49.49. $C_{10}H_{15}CN$ $\overline{\Gamma}_2$. Calculated 49.63.

Found %: N 8.48. $C_{11}H_{15}N$. Calculated %: N 8.69.

Fraction II: d_4^{20} 0.9556; n_D^{20} 1.5036; MR_D 48.89 g.

Found %: N 8.50.

Saponification of the nitrile. 3.9 g cyanodipentene and 25 ml 25% potassium hydroxide were heated to boiling until ammonia ceased to come off (17 hours). The nitrile odor was still detectable. The solution was steam-distilled and extracted with ether for removal of neutral substances. The alkaline solution was made acid to congo and extracted with ether. The ether was removed from the extract to leave a residue of 3.0 g. Gram-equivalent found 200.6; calculated for $C_{10}H_{15}COOH$ 180. The oil was subjected to molecular distillation at 0.001 mm when a large portion (1.1 g) came over at a bath temperature of 90-100°. The crystals were drained from the semisolid distillate and pressed on paper; m.p. 39-40°; gram-equiv. 181.6.

Liquid portion: Found %: C 73.1; H 9.1; equiv. 178.6. $C_{10}H_{15}COOH$. Calculated %: C 73.3; H 8.95; equiv. 180.

The liquid and solid portions may be stereoisomers of 6-dipentenylformic acid.

SUMMARY

1. Chlorides (I) and (II) are used as examples to show the possibility of transformation of the chlorterpenes prepared by us into the nitriles of the corresponding terpenyl formic acids.

2. Saponification of the nitriles gave these acids. It is shown that migration of the Δ^3-double bond to the Δ^4-position [10] does not take place during synthesis of myrtenyl formic acid.

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Received April 17, 1951

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SYNTHESIS AND PROPERTIES OF ETHERS OF DISECONDARY γ-GLYCOLS

I. PREPARATION OF THE METHYL AND ETHYL ETHERS OF DIPHENYLBUTYNEDIOL

Yu. S. Zalkind*, E. D. Venus-Danilova and V. N. Mikhailova

Ethers of disecondary γ-glycols of the acetylenic, ethylenic and saturated series have scarcely been investigated.

The acetylenic derivatives only became accessible to investigation after the discovery by Zh. I. Iotsich [1] of a method of synthesis of γ-glycols via organomagnesium compounds. Apart from this method, ditertiary γ-glycols are obtained as by-products in the condensation of acetylene with ketones in presence of potassum hydroxide by A. E. Favorsky's reaction [2].

The simplest method of synthesis of ethers of acetylenic γ-glycols is the direct action of monohydric alcohols on a glycol in presence of an acidic catalyst, as first carried out by G. A. Arbuzov [3]. The author used a small amount of iodine as catalyst on the assumption that hydriodic and hypoiodous acids are always formed by the action of water (always present in the alcohol) during the etherization of the glycols. The correctness of this assumption was later confirmed by Yu. S. Zalkind and P. S. Bataev [4].

A large number of ethers of disecondary acetylenic γ-glycols containing aliphatic and aromatic radicals were prepared by Sh. Mamedov who used concentrated sulfuric acid as catalyst. It is necessary to point out that ethers are by no means invariably formed by heating glycols with the appropriate alcohols in presence of a small quantity of acid.

For example, according to Yu. S. Zalkind, E.D. Venus-Danilova and V. I. Ryabtseva [6, 7, 8], when unsymmetrical dimethyldiphenylbutynediol is heated with ethyl alcohol in presence of various amounts of sulfuric acid the anticipated ether was not obtained, but instead a diketone, furanone and ethoxydihydropyran-2,5. When attempts were made to prepare the phenyl ethers of tetraphenylbutynediol [9], tetramethylbutynediol [10] and unsymmetrical dimethyldiphenylbutynediol [6] in presence of sulfanilic acid, products of condensation of the respective glycols were isolated as well as products of their further transformation.

In the present communication the synthesis is described of the full methyl and ethyl ethers of diphenylbutynediol and their reduction to the corresponding ethers of diphenylbutenediol and diphenylbutanediol.

$$C_6H_5CH(OR)-C\equiv C-CH(OR)-C_6H_5 \xrightarrow[Pd]{H_2} C_6H_5CH(OR)-CH=CH-CH(OR)-C_6H_5 \xrightarrow[Pt]{H_2}$$

$$\rightarrow C_6H_5CH(OR)-CH_2-CH_2-CH(OR)-C_6H_5\text{, where: } R=OCH_3,\ OC_2H_5.$$

The methyl and ethyl ethers of diphenylbutynediol were prepared by Mamedov's method from the corresponding alcohols and diphenylbutynediol with m.p. 140-142°, synthesized by Iotsich's method [11] from dimagnesiumdibromo acetylene and acetaldehyde. It should be noted that when following the instructions recommended by Mamedov for the synthesis of diphenylbutynediol, we were able to obtain a 70% yield only by using a smaller amount of sulfuric acid, and when prolonging the duration of the reaction.

The ethers of diphenylbutynediol prepared by us were identical with those previously described by Mamedov; however, when the ethers were very carefully dried and subjected to repeated vacuum fractionation, we were unable to get a negative reaction with the organomagnesium compound, pointing to contamination with partial ethers. The ethers of diphenylbutynediol prepared by us were therefore reacted with dialkyl magnesium halides. By this means the partial ethers were precipitated as magnesium alcoholates while the full ethers remained in solution. A similar purification was previously undertaken by Yu. S. Zalkind and I. P. Khazova [12] when synthesizing the ethers of tetramethylbutynediol.

After decomposing the organomagnesium complex we isolated a faint-yellow liquid with a pleasant odor corresponding to the partial ethyl ether of diphenylbutynediol (II).

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* Deceased.

$C_6H_5CH(OC_2H_5)-C\equiv C-CHOH-C_6H_5$ (II). $C_6H_5CH(OCH_3)-C\equiv C-CH(OCH_3)C_6H_5$ (I),
$C_6H_5CH(OC_2H_5)-C\equiv C-CH(OC_2H_5)C_6H_5$ (III)

The full methyl (I) and ethyl (III) ethers prepared by us by the above procedure are oily liquids with a faint-yellow color.

The chemically pure full ethers of diphenylbutynediol react with potassium permanganate and are oxidized to the corresponding alkoxy acid and to benzoid acid. In an acid medium they are hydrolyzed to form the original glycol.

Bromination of the ethers results in addition at the triple bond of only two bromine atoms with formation of the corresponding dibromides which are distinguished by exceptional stability to the action of potassium permanganate solution, bromine water and hydrogen.

The full ethers of diphenylbutenediol and diphenylbutanediol were prepared by hydrogenation of the corresponding ethers of diphenylbutynediol in presence of colloidal palladium and platinum black. The ethers of both the olefinic and the saturated series were isolated.

The ethers of diphenylbutenediol are oily, light-yellow liquids, readily oxidized by potassium permanganate solution. They are at once decolorized by bromine water. The ethers obtained by addition of 4 atoms of hydrogen to the glycol molecule are likewise light-yellow, oily liquids.

It was established that in the hydrogenation of the ethers of diphenylbutynediol in identical conditions with the same amount of catalyst, the full methyl ether is hydrogenated more rapidly than the full ethyl ether.

EXPERIMENTAL

I. Synthesis of Methyl and Ethyl Ethers of Diphenylbutynediol

To diphenylbutynediol with m.p. 140-142°, obtained by the Iotsich method, was added the alcohol containing a small amount of concentrated sulfuric acid (s.g. 1.83). After heating and stirring, the reaction mass was neutralized with anhydrous sodium carbonate. The reaction products were extracted with ether, washed with water, dried with sodium sulfate and vacuum-distilled. Results are in Table 1.

TABLE 1

No. of expt.	Amount of diphenylbutynediol (in g)	CH_3OH (in ml)	C_2H_5OH (in ml)	H_2SO_4 (in ml)	duration of reaction in hrs	Temperature Experimental (in °)	Temperature Of boiling of ether	Yield of ether (in g)	Yield of ether (in %)
1	10	50	–	2.5	24	60-65	172-175/3 mm	8.0	71.6
2	10	50	–	3.0	24	60-65	180-184/4 mm	8.0	71.6
3	5	–	40	2.0	24	70-80	185-190/5 mm	4.7	76.17
4	10	–	50	5.0	15	70-80	182-190/5 mm	3.85	31.20

II. Separation of the Mixture of Full and Partial Ethers of Diphenylbutynediol

The percentage of partial ether in the mixture was determined and the mixture dissolved in three times the volume of dry ether; dropwise addition, under continuous stirring, was then made to the cooled organomagnesium compound. At the termination of the reaction the ethereal solution contained the full ether and the precipitate contained the partial ether in the form of an organomagnesium complex. The product obtained after decomposition of the organomagnesium complex of the partial methyl ether of diphenylbutynediol was not investigated, due to the minute amount. From the ethereal layer was isolated a fraction with b.p. 168-170° at 2 mm, corresponding to the full methyl ether of diphenylbutynediol. In similar purification of the ethyl ether of diphenylbutynediol, a fraction with b.p. 193-194° at 3.5 mm was isolated which corresponded to the partial ethyl ether; from the ethereal layer was isolated a fraction with b.p. 188-190° at 2 mm, corresponding to the full ethyl ether of diphenylbutynediol.

Examination of the 168-170° (2 mm) fraction. (Full methyl ether of diphenylbutynediol.

0.2005 g substance: 0.5950 g CO_2; 0.1225 g H_2O. 0.2101 g substance: 0.6233 g CO_2; 0.1314 g H_2O. Found %: C 80.93, 80.91; H 6.83, 6.99. $C_{18}H_{18}O_2$. Calculated %: C 81.20; H 6.76.

Zeisel determination of methoxy groups: 0.1002 g substance: 0.1760 g AgI. Found %: CH_3O 23.24. $C_{18}H_{18}O_2$. Calculated %: CH_3O 23.31.

Determination of specific gravity and molecular refractinn: d_{20}^{20} 1.0800; n_D^{20} 1.5600. Found: MR_D 79.64. $C_{18}H_{18}O_2$. Calculated: MR_D 79.41.

Chugaev-Tserevitinov determination of hydroxyl groups gives negative results.

Examination of 193-194° (3.5 mm) fraction. (Partial ethyl ether of diphenylbutynediol.)

0.2521 g substance: 0.7500 g CO_2; 0.1590 g H_2O. 0.2201 g substance: 0.6538 g CO_2; 0.1369 g H_2O. Found %: C 81.13, 81.01; H 7.05, 6.96. $C_{18}H_{18}O_2$. Calculated %: C 81.20; H 6.77.

Molecular weight determination: 0.1505 g substance: 29.5 g C_6H_6: Δt 0.10°. 0.2003 g substance. 19.8 g C_6H_6: Δt 0.20°. Found: M 260.2; 258. $C_{18}H_{18}O_2$. Calculated: M 266.

Zeisel determination of ethyoxyl groups: 0.1362 g substance: 0.1200 g AgI. Found %: C_2H_5O 16.89. $C_{18}H_{18}O_2$ Calculated %: C_2H_5O. 16.92.

Specific gravity and molecular refraction: d_{20}^{20} 1.0608; n_D^{20} 1.5425. Found: MR_D 78.91. $C_{18}H_{18}O_2$. Calculated MR_D 79.29.

Terentev determination of hydroxyl groups: 0.0720 g substance: 6.2 ml CH_4 (18°, 763 mm). Found: ν_0 CH_4 5.7 ml; % OH 5.87. $C_{18}H_{17}O(OH)$. Calculated: CH_4 6.0 ml; % OH 6.39.

The substance with b.p. 193-194° at 3.5 mm corresponds to the partial ethyl ether of diphenylbutynediol and is a light-yellow liquid with a pleasant odor. It dissolves readily in organic solvents. Hydrolysis of the ether with 10% sulfuric acid gives the original glycol.

Examination of the fraction with b.p. 188-190° at 2 mm. (Full ethyl ether of diphenylbutynediol).

0.2101 g substance: 0.6280 g CO_2; 0.1421 g H_2O. 0.2302 g substance: 0.6880 g CO_2; 0.1570 g H_2O. Found %: C 81.52, 81.51; H 7.51, 7.63. $C_{20}H_{22}O_2$. Calculated %: C 81.63; H 7.48.

Molecular weight determination: 0.1005 g substance; 11.40 g C_6H_6; Δt 0.15°. 0.2001 g substance; 12.30 C_6H_6: Δt 0.28°. Found: M 299.7, 296.3. $C_{20}H_{22}O_2$. Calculated: M 294.

Zeisel determination of ethoxyl groups: 0.2150 g substance: 0.3401 g AgI. Found %: C_2H_5O 30.32. $C_{20}H_{22}O_2$. Calculated %: C_2H_5O 30.61.

Specific gravity and molecular refraction: d_{20}^{20} 1.0469; n_D^{20} 1.5455. Found: MR_D 88.85. $C_{20}H_{22}O_2$. Calculated: MR_D 88.64.

The full ethyl ether of diphenylbutynediol is a light-yellow oily liquid with a floral odor.

Oxidation of substance with b.p. 168-170° at 2 mm. 3 g of the full methyl ether of diphenylbutynediol was oxidized with 4.7 g potassium permanganate (calculated for four atoms of oxygen per molecule of ether) in presence of 0.5 g potassium carbonate. The oxidizing agent was added in the form of 1% solution dropwise with stirring at room temperature. Duration of oxidation was 3 hours. Ether extraction was performed at the conclusion of the reaction. No neutral products were identified. Benzoic acid with m.p. 121° came down from the filtrate after concentration and acidification with 10% sulfuric acid It did not depress the melting point of an authentic specimen of benzoic acid.

From the acids which were difficultly volatile in steam was isolated a yellowish viscous oil, part of which crystallized in the form of rods after prolonged standing. It was impossible, however, to determine the melting point because the crystals could not be isolated in the pure form. A portion of the obtained acid was converted into the silver salt via the ammonium salt.

0.2101 g salt: 0.3037 g CO_2; 0.0647 g H_2O; 0.0825 g Ag. 0.1521 g salt : 0.2197 g CO_2; 0.0476 H_2O; 0.0596 g Ag. Found %: C 39.42, 39.39; H 3.44, 3.50; Ag 39.26, 39.18. $C_9H_9O_2Ag$. Calculated %: C 39.58; H 3.30; Ag 39.53.

The prepared silver salt corresponds to the salt of methoxyphenylacetic acid. According to the literature [13], this acid is a slowly solidifying oil.

Oxidation of substance with b.p. 188-190° at 2 mm. 3 g of the full ethyl ether of diphenylbutynediol was oxidized with 4.3 g potassium permanganate (amount calculated for four atoms of oxygen per molecule of ether) in the form of 1% solution. Oxidation was effected in the same way as for the methyl ether of diphenylbutynediol. Duration of the reaction was 4.5 hours. The reaction products were extracted by the usual method. In addition to benzoic acid, an acid was isolated in the form of a yellow, viscous oil which was converted to the silver salt.

0.0592 g salt: 0.0899 g CO_2; 0.0183 g H_2O; 0.224 g Ag. Found %: C 41.41; H 3.45; Ag 37.84. $C_{10}H_{11}O_3Ag$. Calculated: C 41.83; H 3.83; Ag 37.60.

The acid corresponds to ethoxyphenylacetic acid. According to the literature [13], this acid is a viscous oil and forms a silver salt which does not darken in the air.

III. Bromination of the Full Methyl and Ethyl Ethers of Diphenylbutynediol

Into 2 g of the full methyl ether of diphenylbutynediol dissolved in 30 ml dry chloroform was run 12 ml 10% solution of bromine in dry chloroform (calculated for two atoms of bromine per molecule of the ether). Bromination required 2.5 hours at a temperature of 20-30°.

No evolution of hydrogen iodide was observed. Any bromine not entering into reaction was bound by washing with sodium carbonate solution and then with water. After drying the ether-chloroform solution and distilling off the solvents, a liquid was obtained which crystallized on standing. It melted at 145-146° after recrystallization from ethyl alcohol.

When bromination was carried out with the amount of bromine calculated for four atoms of bromine per molecule of glycol ether, a similar product with m.p. 145-146° was isolated in the form of fine white crystals.

0.1398 g substance: 0.1223 g AgBr. Found %: Br 37.23. $C_{18}H_{18}O_2Br_2$. Calculated %: Br 37.53.

Molecular weight determination: 0.0690 g substance; 16.50 g C_6H_6: Δt 0.05°. 0.0722 g substance: 17.55 g C_6H_6: Δt 0.05°. Found: M 427.0, 420.0. $C_{18}H_{18}O_2Br_2$. Calculated: M 425.8.

Zeisel determination of methoxyl groups: 0.0638 g substance: 0.0670 g AgI. Found %: CH_3O 13.89. $C_{18}H_{18}O_2Br_2$. Calculated %: CH_3O 14.58.

The obtained dibromide was readily soluble in benzene and chloroform and did not decolorize bromine water and potassium permanganate solution. By heating it with zinc dust in alcoholic solution for 12 hours there was obtained (in addition to unchanged dibromide) a small amount of the corresponding ether.

Bromination of the full ethyl ether was effected in similar condition. Reaction with both two and four atoms of bromine gave one and the same liquid dibromide which decomposed when distilled in vacuum. Analysis was therefore performed immediately after drying and driving off the solvent.

0.1116 g substance: 0.0946 g AgBr. 0.1564 g substance: 0.1308 g AgBr. Found %: Br 36.07, 35.59. $C_{20}H_{22}O_2Br_2$. Calculated %: Br 35.22.

Molecular weight determination: 0.1824 g substance; 20.10 g C_6H_6; Δt 0.10. Found: M 462.8. $C_{20}H_{22}O_2Br_2$. Calculated: M 453.8.

The obtained liquid dibromide does not decolorize bromine water or potassium permanganate solution.

IV. Hydrogenation of the Methyl and Ethyl Ethers of Diphenylbutynediol in Presence of Colloidal Palladium and Platinum Black

Colloidal palladium was prepared by Paal's method, platinum black by Loew's method [15]. The hydrogenation catalysts were always freshly prepared; their activity was tested by hydrogenation of tetramethylbutynediol. Electrolytic hydrogen was used.

The hydrogenation procedure and the isolation and purification of the products have been described in numerous papers by Yu. S. Zalkind and co-workers [16, 17, 18, 19, 20].

The hydrogenation products were investigated after addition of two atoms of hydrogen per molecule of ether and also after addition of four atoms of hydrogen.

1) Examination of product of hydrogenation of the full methyl ether of diphenylbutynediol.

a) After addition of two atoms of hydrogen (colloidal palladium catalyst). The product of incomplete hydrogenation of the methyl ether of diphenylbutynediol is a light-yellow, fairly mobile liquid with a rather pleasant odor, b.p. 210-211° at 5 mm, readily soluble in organic solvents. It energetically decolorizes bromine water and potassium permanganate solution. No hydroxyl groups were detected by the Chugaev-Tserevitinov method.

0.1302 g substance: 0.3840 g CO_2; 0.0889 g H_2O. 0.1221 g substance: 0.3603 g CO_2; 0.0836 g H_2O. Found %: C 80.43, 80.47; H 7.64, 7.66. $C_{18}H_{20}O_2$. Calculated %: C 80.60; H 7.46.

Molecular weight determination: 0.1542 g substance; 14.20 g C_6H_6; Δt 0.21°. Found: M 263.7. $C_{18}H_{20}O_2$. Calculated: M 268.0.

Zeisel determination of methoxyl groups: 0.1012 g substance: 0.1750 g AgI. Found %: CH_3O 22.88. $C_{18}H_{20}O_2$. Calculated %: CH_3O 23.13.

Specific gravity and molecular refraction: d_{20}^{20} 1.0555; n_D^{20} 1.5570. Found: MR_D 81.00. $C_{18}H_{20}O_2$. Calculated: MR_D 80.96.

Oxidation of the product of hydrogenation with b.p. 210-211° at 5 mm. 3 g of hydrogenation product was oxidized with 4.7 g potassium permanganate (calculated for four atoms of oxygen per molecule of hydrogenation product) in the form of 1% aqueous solution. Oxidation was first performed under cooling with iced water and later at room temperature. The reaction period was $2\frac{1}{2}$ hours.

The oxidation products were isolated by the usual procedure and corresponded to benzoic and methoxyphenylacetic acids (see oxidation of full methyl ether of diphenylbutynediol).

b) After addition of four hydrogen atoms (platinum black catalyst). The product of full hydrogenation of the full methyl ether is a light-yellow, mobile liquid with b.p. 150-155° at 2 mm; it has a very faint odor; it is readily soluble in organic solvents. It does not decolorize bromine water or potassium permanganate solution.

0.1542 g substance: 0.4513 g CO_2; 0.1135 g H_2O. 0.2031 g substance: 0.5948 g CO_2; 0.1501 g H_2O. Found %: C 79.81, 79.86; H 8.23, 8.27. $C_{18}H_{22}O_2$. Calculated %: C 80.00; H 8.14.

Molecular weight determination: 0.2411 g substance; 23.80 g C_6H_6; Δt 0.19°. Found: M 271.9. $C_{18}H_{22}O_2$. Calculated: M 270.0.

Zeisel determination of methoxyl groups: 0.1620 g substance: 0.2781 g AgI. Found %: CH_3O 22.71. $C_{18}H_{22}O_2$. Calculated %: CH_3O 22.96.

Specific gravity and molecular refraction: d_{20}^{20} 1.0340; n_D^{20} 1.5380. Found: MR_D 81.65. $C_{18}H_{22}O_2$. Calculated: MR_D 81.43.

2) Investigation of the product of hydrogenation of the full ethyl ether.

a) After addition of two atoms of hydrogen (colloidal palladium catalyst). The product of incomplete reduction of the ethyl ether of diphenylbutynediol is a light yellow liquid boiling at 173-174° at 3 mm; readily soluble in organic solvents. It decolorizes bromine water and potassium permanganate solution.

0.1531 g substance: 0.4541 g CO_2; 0.1133 g H_2O. Found %: C 80.89; H 8.28. $C_{20}H_{24}O_2$. Calculated %: C 81.08; H 8.11.

Molecular weight determination: 0.1251 g substance; 14.50 g C_6H_6; Δt 0.15°. Found: M 293.3. $C_{20}H_{24}O_2$. Calculated: M 296.0.

Determination of ethoxyl groups (Zeisel): 0.1849 g substance: 0.2920 g AgI. Found %: C_2H_5O 30.26. $C_{20}H_{24}O_2$. Calculated %: C_2H_5O 30.41.

Specific gravity and molecular refraction: d_{20}^{20} 1.0260; n_D^{20} 1.5388. Found: MR_D 90.35. $C_{20}H_{24}O_2$. Calculated: MR_D 90.20.

Oxidation of the partial hydrogenation product was performed as for the oxidation of the full ethyl ether of diphenylbutynediol. The reaction period was 3 hours. Analogous products were isolated: benzoic acid and ethoxyphenylacetic acid which was characterized as the silver salt.

0.1425 g substance: 0.2179 g CO_2; 0.0508 g H_2O; 0.0534 g Ag. Found %: C 41.70; H 3.98; Ag 37.47. $C_{10}H_{11}O_3Ag$. Calculated %: C 41.83; H 3.83; Ag 37.63.

b) After addition of four hydrogen atoms (platinum black catalyst). The product of full hydrogenation of the ethyl ether is a light-yellow liquid boiling at 120-124° at 3 mm. It does not decolorize bromine water and potassium permanganate solution.

0.1331 g substance: 0.3921 g CO_2; 0.1059 g H_2O. Found %: C 80.34; H 8.84. $C_{20}H_{28}O_2$. Calculated %: C 80.54; H 8.72.

Ethoxyl groups determination (Zeisel): 0.1542 g substance: 0.2420 g AgI. Found %: C_2H_5O 30.07. $C_{20}H_{26}O_2$. Calculated %: C_2H_5O 30.20.

Specific gravity and molecular refraction: d_{20}^{20} 1.0210. n_D^{20} 1.5380. Found: MR_D 91.30. $C_{20}H_{26}O_2$. Calculated: MR_D 90.67.

SUMMARY

1. The following compounds were synthesized and characterized: 1,4-Diphenyl-1,4-dimethoxybutyne-2; 1,4-diphenyl-1,4-dimethoxybutene-2; 1,4-diphenyl-1,4-dimethoxybutane; 1,4-diphenyl-1,4-diethoxybutyne-2; 1,4-diphenyl-1,4-diethoxybutene-2; 1,4-diphenyl-1,4-diethoxybutane; and 1,4-diphenyl-1-ethoxybutyne-2-ol-4.

2. The bromination of the methyl and ethyl ethers of diphenylbutynediol was investigated. Bromine was found to combine in the proportion of two atoms per molecule of the glycol.

3. The dibromides prepared by bromination of the methyl and ethyl ethers of diphenylbutynediol were isolated and characterized.

4. Hydrogenation of the methyl and ethyl ethers of diphenylbutynediol with colloidal platinum gives the corresponding ethers of the olefinic series, and hydrogenation with platinum black gives the ethers of the saturated series.

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Received June 13, 1951

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* See Consultants Bureau English translation, p. 593.

** See Consultants Bureau English translation, p. 2317.

*** See Consultants Bureau English translation, p. 2309.

**** See Consultants Bureau English translation, p. 923.

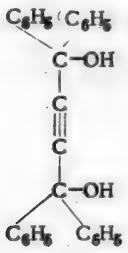
THE REACTION OF 2,5-DIPHENYLHEXYNE-3-DIOL-2,5 (SYMMETRICAL DIMETHYLPHENYLBUTYNEDIOL) WITH PHENOL IN PRESENCE OF SULFANILIC ACID

Yu. S. Zalkind* and G. M. Kharkharova

Yu. S. Zalkind, V. K. Teterin and S. G. Kuznetsov [1] were the first to show that acetylenic γ-glycols are capable of condensing with phenol in presence of acid catalysts. It was established that tetraphenylbutynediol (I), which only contains aromatic radicals attached to the hydroxyl carbon, condenses with phenol in presence of sulfanilic acid to form derivatives of benzfulvene, dihydrofuran and indenechroman.

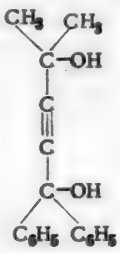
Tetramethylbutynediol (II), containing only aliphatic radicals [2], and unsymmetrical dimethyldiphenylbutynediol (III), whose methyl groups are concentrated at one carbon atom and the phenyl groups at another [3], react with phenol predominantly with formation of dihydrofuran derivatives.

The symmetrical dimethyldiphenylbutynediol which we have investigated contains both aliphatic and aromatic radicals at the same tertiary alcoholic carbon atom (IV).



(I)

(II)



(III)

(IV)

Both of its isomers react with phenol in presence of sulfanilic acid in a medium of dry benzene to form identical condensation products. The reaction proceeds fairly readily with loss of about two molecules of water per molecule of glycol and is completed in the course of an hour.

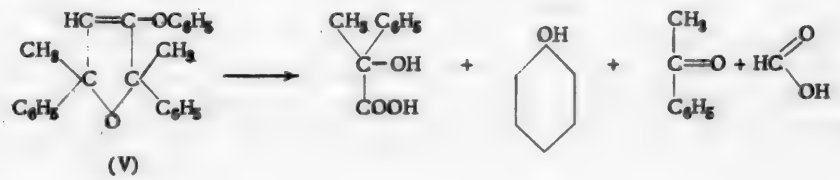
After steam-distillation of the excess of phenol and solvent, a low-melting oil was obtained from which, not without difficulty, we succeeded in isolating six substances with a total yield of about 70%.

The properties of these substances, and also their ultraviolet and visible spectral curves (Figure 1) showed that to none of these compounds could a structure close to that of the original glycol be assigned.

Three of our isolated products appear to have structures similar to the products of condensation of tetraphenylbutynediol with phenol [1].

A light-yellow oil obtained in a yield of about 6% was vacuum-distilled (5-10 mm) at 230-260°. In elementary analysis and molecular weight it corresponded to $C_{24}H_{22}O_2$, indicating the addition of one molecule of phenol to glycol with elimination of a molecule of water.

The substance did not contain hydroxyl groups and did not react with an alcoholic solution of semicarbazide. When digested with hydrogen iodide it split up with formation of phenol, demonstrating the presence of a phenoxy group. On the basis of these data the substance was assigned the structure of 2,5-dimethyl-2,5-diphenyl-3-phenoxydihydrofuran-2,5 (V).



(V)

* Deceased.

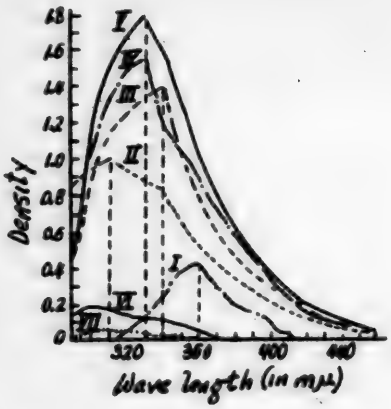


Fig. 1. Curves of absorption spectra of isomers of the original glycol and of products of their condensation with phenol.

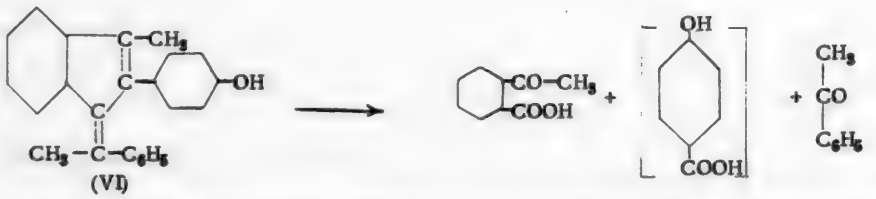
I - lemon-yellow substance with m.p. 220-220.5°;
II - light-yellow substance with m.p. 154-160°;
III - orange substance with m.p. 80-82°;
IV - yellow substance with m.p. 125-127°;
V - yellow substance with m.p. about 50°;
VI - dimethyldiphenylbutynediol with m.p. 160°;
VII - dimethyldiphenylbutynediol with m.p. 125-127°.

The structure was confirmed by oxidation with potassium permanganate in acetone [1]. Oxidation did not proceed to completion, part of the substance being recovered unchanged. Acetophenone and phenol were found in the neutral products of oxidation; formic and methylphenylglycollic acids in the acidic products.

The composition of the oxidation products thus confirmed the proposed structural formula.

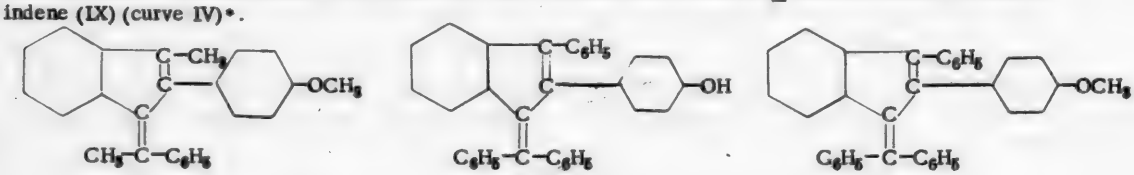
The yellow crystalline substance with m.p. 125-127° corresponded in composition to $C_{24}H_{20}O$, pointing to addition to the glycol of one molecule of phenol with elimination of two molecules of water. The yield was 15-16%.

Its color (absorption maximum at 330 mμ) (Fig. 1, curve IV), the ability to decolorize bromine water and potassium permanganate solution, the formation of a crimson coloration in concentrated sulfuric acid all indicated that this compound contained the benzfulvene group. The Chugaev-Tserevitinov reaction showed the presence of one hydroxyl group. Its ability to form a phenolate pointed to its phenolic character. On the basis of the foregoing facts the structure can be assumed to be 1-methylphenylmethylene-2-(p-hydroxyphenyl)-3-methylindene (VI):



(VI)

This structure was confirmed by oxidation. Among the oxidation products were found acetophenone, acetylbenzoic acid and, apparently, phthalic acid; p-hydroxy-benzoic acid was decomposed in these conditions. The isolated oxidation products were not inconsistent with the proposed structure. Support for the structure (VI) is also provided by a comparison of its spectral curve (curve I, Fig. 1) with the curves of its methoxy derivative (VII) (Fig. 2, curve II), which was prepared by reaction of anisole with 2,5-diphenylhexyne -3-diol-2,5 and with the curves of two compounds whose structures are authenticated: 1-diphenylmethylene-2-(p-hydroxyphenyl)-3-phenylindene (VIII) (curve III) and 2-diphenylmethylene-2-(p-methoxyphenyl)-3-phenylindene (IX) (curve IV)*.



(VII) (VIII) (IX)

Comparison of the absorption spectral curves (Fig. 2) showed that all four substances are very similar in structure. The maxima of the first two (330 mμ and 320 mμ) are in a shorter wave portion of the spectrum compared to the maxima of the other two (370 mμ and 360 mμ). Such a shift in the absorption band was also

* The benzfulvene derivatives (VIII), (IX) and (XI) were kindly placed at our disposal by S. G. Kuznetsov.

to be expected after replacement of two methyl groups by phenyl groups.

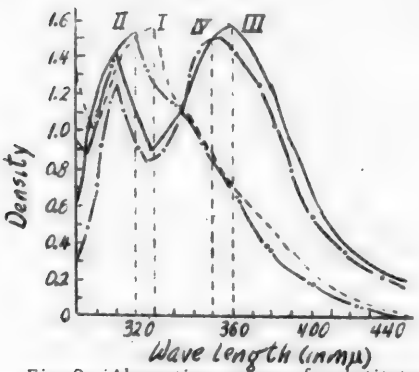


Fig. 2. Absorption curves of substituted benzfulvenes.
I. 1-methylphenylmethylene-3-(p-hydroxyphenyl)-3-methylindene (yellow substance with m.p. 125-127°)(formula VI); II. 1-methylphenylmethylene-2-(p-methoxyphenyl)-3-methylindene (formula VII); III. 1-diphenylmethylene-2-(p-hydroxyphenyl)-3-phenylindene (formula VIII); IV. 2-diphenylmethylene-2-(p-methoxyphenyl)-3-phenylindene (formula IX).

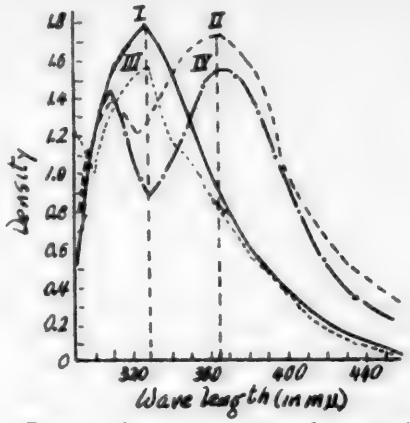
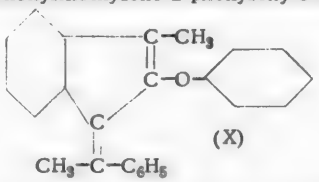


Fig. 3. Absorption spectra of some indene derivatives.
I. 1-methylphenylmethylene-2-phenoxy-3-methylindene (formula X); II. 1-diphenylmethylene-2-phenoxy-3-phenylindene (formula XI); III. 1-methylphenylmethylene-2-(p-hydroxyphenyl)-3-methylindene (formula VI); IV. 1-diphenylmethylene-2-(p-hydroxyphenyl)-3-phenylindene (formula VIII).

The absorption curves of the ethers (Fig. 2, curves II and IV) and their oxy compounds (Fig. 2, curves I and III) are similar in character, but their maxima are shifted to the left.

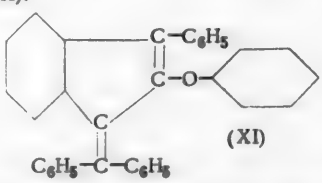
The yellow amorphous substance obtained in a yield of 6-10% melted at about 50°. It is apparently the isomeric 1-methylphenylmethylene-2-(p-hydroxyphenyl)-3-methylindene (VI). Its absorption curve is similar to the curve of 1-methylphenylmethylene-(2-p-hydroxyphenyl)-3-methylindene (Fig. 1, curves IV and V).

The maxima of these curves are at the same wave length (330 mμ). The absence of hydroxyl, the presence of a phenoxy group and the red coloration in concentrated sulfuric acid enable us provisionally to assign to it the structure of 1-methylphenylmethylene-2-phenyloxy-3-methylindene (X).



(X)

:



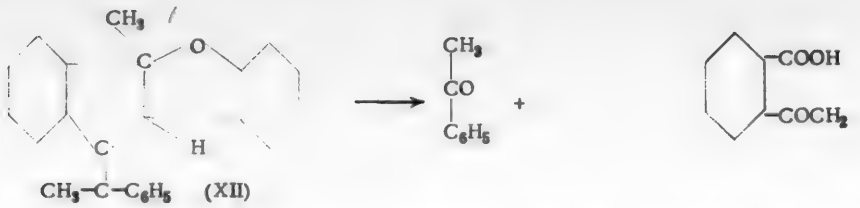
(XI)

All the curves plotted in Figure 3 are similar in character, and thus point to similar structures of these compounds.

The remaining substances isolated from the reaction mass differ in properties both from one another and from the above-noted products. Their absorption curves (Fig. 1, curves I, II, and III) differ both in form and in position of maxima (360, 310, 340 mμ).

One of these is in the form of lemon-yellow crystals (Fig. 1, curve I) with m.p. 220-220.5°, yield 1.5%.

The analytical data and molecular weight agree with the formula $C_{24}H_{20}O$. This compound is the most deeply colored (maximum at 360 mμ) (Fig. 1, curve I). It is sparingly soluble in concentrated sulfuric acid and almost insoluble in all organic solvents. Its solutions do not exhibit the fluorescence which is characteristic of indenechroman derivatives. [1]. The absence of hydroxyl, carbonyl and phenoxy groups suggest that the oxygen in the molecule is present in a ring. This compound may have been formed by addition of phenol in the ortho-position followed by closure of the cumarone ring with formation of 2-methyl-1'-methylphenylmethylene-(2', 3': 2,3-indeno)cumaran (XII):

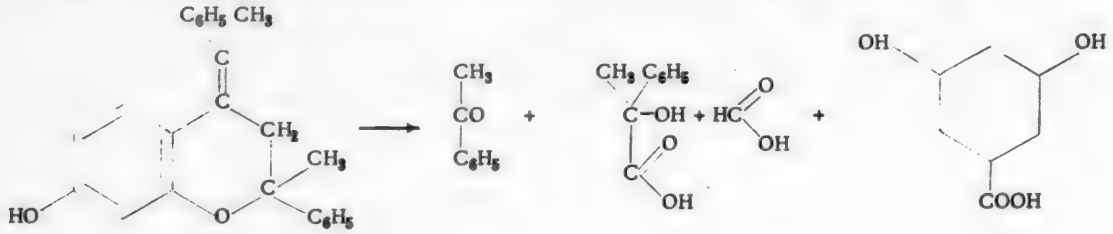


(XII)

Such a structure explains the conversion of the product by hydriodic acid into a substance giving a blue fluorescence. In the oxidation products were detected acetophenone, acetylbenzoic acid and an acid with m.p. 115-118°.

Another product was a light-yellow amorphous substance (yield up to 10%) (Fig. 2, curve II), which melted with decomposition at 154-160°. Its molecular and elementary composition agreed with the formula $C_{72}H_{68}O_3$. It contained a phenolic hydroxyl group. The structure was not elucidated.

Finally, the orange substance with m.p. 80-82° corresponded in elementary formula and molecular weight to $C_{24}H_{22}O_2$. It did not contain phenoxy or carbonyl groups. One oxygen was in a hydroxyl group which bore a phenolic character. Exploratory oxidation of the substance showed that the neutral products contain acetophenone and the acid ones (in addition to formic acid and methylphenylglycollic acid), an acid which resembled 2,4-dihydroxybenzoic acid in being easily brominated (bromide with m.p. 80-83°) and in giving a red coloration with iron chloride. Its silver salt easily decomposed. The evidence did not justify assigning to it a dihydrofuran structure. It is possibly 2-methylphenyl-4-methylphenylmethylene-7-hydroxy-2,3-dihydrobenzpyran (XIII):

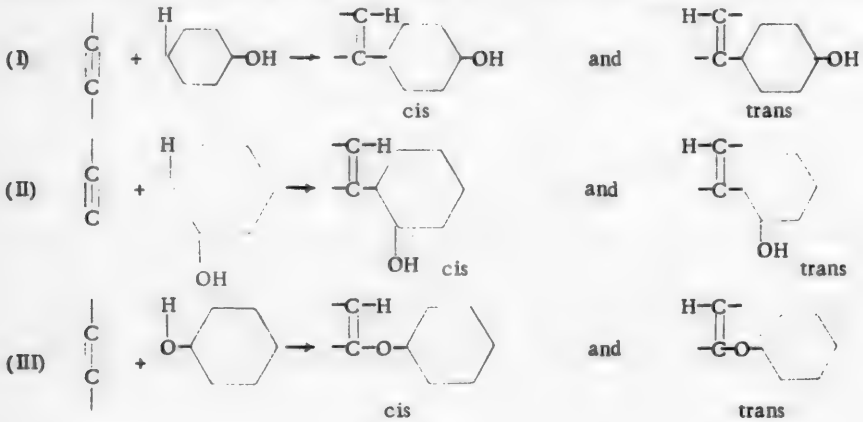


(XIII)

Oxidation of such a compound would result in the occurrence of 2,4-dihydroxybenzoic acid among the oxidation products.

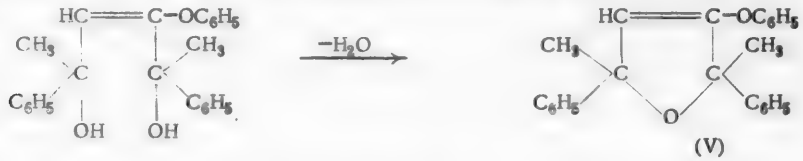
Formation of the above-mentioned products of condensation of symmetrical dimethyldiphenylbutynediol with phenol apparently proceeds, as in the case of tetraphenylbutynediol (I), via the addition of phenol at the triple bond.

Addition of phenol may take place in three ways: at the para- and ortho-carbon atom (since there is a higher electronic density at these points) and at the hydroxyl oxygen which has a free electron pair:



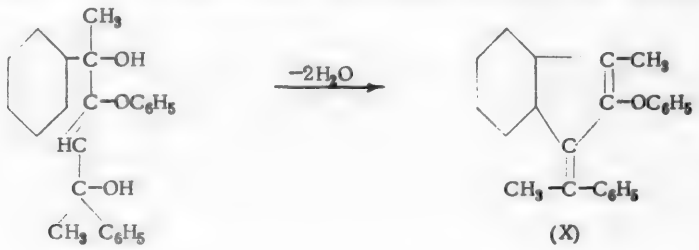
The intermediate products of addition of phenol to the glycol can exist in cis- and trans-forms. In the reaction conditions these products tend to pass into the more stable cyclic compounds. The cis-form is susceptible to cyclization to γ-oxides due to the proximity of the two hydroxyl groups.

Thus the formation of 2,5-dimethyl-2,5-diphenyl-3-phenoxydihydrofuran-2,5 (V) would appear to proceed via the cis-form of the vinyl ether (product of addition of phenol at the triple bond of the glycol; scheme III):



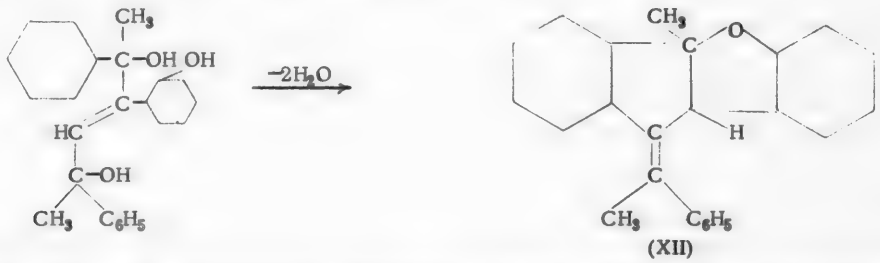
(V)

1-Methylphenylmethylene-2-phenoxy-3-methylindene (X) is possibly formed via the trans-form of the vinyl ether:



(X)

1-Methylphenylmethylene-2-(p-hydroxyphenyl)-3-methylindene (VI) is derived from the trans-form of the products of addition of phenol in the p-position (scheme II). When addition occurs in the o-position, closure of both the indene and cumarone ring takes place according to the scheme:



(XII)

The trans-form is possibly the intermediate in formation of products of dehydration, of pyran derivatives, of resins, etc.

Closure of the pyran ring is possible at the expense of the double bond of the phenolic nucleus activated by the presence of the phenolic hydroxyl.

Consequently the reaction of phenol with symmetrical dimethyldiphenylbutynediol gives products some of which are similar in structure to those resulting from the phenol-tetraphenylbutynediol condensation and some of which are different in structure.

It transpired that the yield of products of transformation of the cis-form in the case of tetraphenylbutynediol is 3%, that in the case of unsymmetrical dimethyldiphenylbutynediol is up to 85%, that of symmetrical dimethyldiphenylbutynediol is 6.10%, and that of tetramethylbutynediol is about 40%.

We see, therefore, that the largest amount of cis-derived products is formed in the case of the unsymmetrical glycol molecule. In the symmetrical glycols the replacement of alkyl groups by aryls leads to a drop in yield of these transformation products.

On the basis of the foregoing observations it follows that the behavior of acetylenic γ-glycols largely depends on their structure, i.e., on the character and arrangement of the radicals attached to the carbon atom linked to the hydroxyl group.

The joint presence of methyl and phenyl groups at one carbon atom facilitates reaction in various directions. These features have been confirmed in work with other compounds [6].

EXPERIMENTAL

Preparation of 2,5-diphenylhexyne-3-diol-2,5 (symm. dimethyldiphenylbutynediol) (IV). The glycol was prepared, as described by Iotsich [4], by the action of acetophenone on acetylene bismagnesium bromide in a medium of dry ether. The inactive steroisomers (i and d + l) of the glycol were resolved by fractional crystallization from ether and alcohol [4]. The total yield of glycol was about 80%; that of the isomer with m.p. 163° was 32%, that of the isomer with m.p. 125-127° was 48%.

Condensation of symmetrical dimethyldiphenylbutynediol with phenol. The reaction was conducted in a V.K. Teterin apparatus [1,5]. It proceeded identically for both of the glycol isomers.

In a round-bottomed flask were placed 13.3 g dimethyldiphenylbutynediol (0.05 mole), 18.8 g phenol (0.2 mole), 0.2 g sulfanilic acid (0.0012 mole) which had been dehydrated at 120-130°, and about 28 ml dry benzene, the latter being the amount calculated to prevent the temperature of the reaction mass from rising above 91°. The mixture was boiled for about an hour. With progressive elimination of water, the color of the reaction mass changed from lemon-yellow to reddish-brown.

A total of 1.67 ml water was given off, which corresponds to 80-85% of the amount calculated for two molecules of water per molecule of glycol. On cooling, the reaction products remained in solution. The precipitate consisted of sulfanilic acid (0.18 g). The reaction products were isolated, after steam-distillation of the excess of phenol and the solvent, in the form of a reddish-brown mass melting at about 40°. The weight of products (17.0 g) roughly corresponded to the addition of one molecule of phenol to one molecule of symm. dimethyldiphenylbutynediol.

The amount of unreacted phenol (13.3 g) also confirmed that one molecule of phenol had reacted.

A total of 880 ml condensation product was obtained. Test with 20 ml sample: 1.06 g tribromphenol. Amount of phenol entering into reaction: found 5.67; calculated 4.7.

The reaction velocity is profoundly influenced by the boiling temperature of the reaction mixture. Hardly any water is eliminated if the boiling temperature is below 86°. At 86° an appreciable amount of water was split off only after 2 hours from the commencement of boiling of the flask contents. Heating at above 91° resulted in serious resinification of the condensation products.

No elimination of water was observed in the absence of sulfanilic acid.

The condensation products were treated with ether when the main bulk went into solution, leaving a small residue of lemon-yellow substances with m.p. 220-220.5° (Fig. 1, curve 1).

A light-yellow powder, decomposing at 154-160°, was isolated from the ethereal solution by fractional precipitation with gasoline. The yield of the substance was 8-10% (Fig. 1, curve II). Evaporation of the filtrate over a long period of time led to separation, first, of an amorphous, orange substance (yield 8-20%), which after purification had m.p. 80-82° (Fig. 1, curve III); this was followed by a yellow crystalline substance (16-17%) with m.p. 125-127° (Fig. 1, curve IV). The residue was fractionated in vacuum to give an oil distilling at 230-260° (5-10 mm) in yield of 6% and an amorphous residue in the flask with m.p. about 50° (Fig. 1, curve V).

The absorption spectra of these substances were examined in a Beckmann spectrophotometer, using 96% ethyl alcohol as solvent. The concentration of the solution was 0.1 g per liter.

1) 2-Methyl-1'-methylphenylmethylene-(2',3':2,3-indeno)cumaran (XII). Beautiful lemon-yellow, tetrahedral prisms (yield 1.5%) with m.p. 220-220.5° (from benzene), difficultly soluble in nearly all organic solvents, in concentrated alkalis and acids. It has two extinctions in polarized light. The absorption maximum is at 360mμ (Fig. 1, curve I). This substance could be separated from the main bulk of glycol-phenol condensation products because of its difficult solubility in ether.

0.1061 g substance: 0.3478 g CO_2; 0.0613 g H_2O. Found %: C 89.39; H 6.45. $C_{24}H_{20}O$. Calculated %: C 88.9; H 6.2. 0.0166 g substance; 0.1626 g camphor: Δt 12.2°. Found: M 335.4. $C_{24}H_{20}O$. Calculated: M 324.3.

The absence of hydroxyl and carboxyl groups was demonstrated in the Chugaev-Tserevitinov reaction and in the reaction with alcoholic semicarbazide solution.

When treated with hydriodic acid, the substance did not regenerate phenol but was converted into another compound which dissolved readily in benzene and gave a blue fluorescence in benzene solution.

Oxidation. To a mixture of 1.0 g substance and 50 ml acetone heated on the water bath was added an acetone solution containing 1.3 g potassium permanganate. Oxidation was completed in 3 hours. The reaction mass was worked up in the usual manner [1]. The neutral products contained acetophenone and a small amount of original substance with m.p. 214-215°. The semicarbazone of the acetophenone melted at 196-199° and did not depress the melting point of an authentic specimen.

The acid products contained o-acetylbenzoic acid with m.p. 113-114° and an acid with m.p. 115-116° (in admixture with benzoic acid and the melting point was depressed by 2°). The acid possessed a pleasant honey-like odor; it crystallized in prisms difficultly soluble in water and very readily soluble in ether. The acid was not further investigated.

Analysis of the silver salt of o-acetylbenzoic acid:

0.0162 g substance: 0.0200 g Ag. 0.0200 g substance: 0.0078 g Ag. Found %: Ag 39.5, 39.0. $C_9H_7O_3Ag$. Calculated %: Ag 39.80.

2) Substance $C_{72}H_{60}O_3$ with m.p. 154-160°.

A light-yellow amorphous powder, decomposing at 154-160° (from alcohol), was isolated by precipitation from the ethereal solution with gasoline. The compound dissolved with difficulty in gasoline, methyl alcohol and ethyl alcohol, readily in ether and benzene. It formed phenolates with caustic alkalis. A brown coloration was developed in concentrated sulfuric acid. Its absorption maximum lies at 310 mμ (Fig. 1, curve II).

0.1025 g substance: 0.3372 g CO_2; 0.0589 g H_2O. Found %: C 89.46; H 6.43. $C_{24}H_{20}O$. Calculated %: C 89.00; H 6.2. 0.1901 g substance: 12 ml CH_4 (16.5°, 765.4 mm). $C_{24}H_{19}(OH)$ Calculated: CH_4 12.72 ml.

0.1270 g substance: 20.52 g benzene: Δt 0.08°. Found: M 1050. $C_{24}H_{20}O$. Calculated: M 324. $C_{72}H_{60}O_3$. Calculated: M 972.

Its structure was not elucidated.

3) 2-Methylphenyl-4-methylphenylmethylene-7-hydroxy-2,3-dihydrobenzpyran (XIII).

After purification the substance was in the form of an orange powder with m.p. 80-82°, readily soluble in ether, benzene, alcohol and acetone, soluble with difficulty in petroleum ether. It forms phenolates with caustic alkalis; it turns concentrated sulfuric acid a dark-yellow color. Absorption maximum at 340 mμ (Fig. 1, curve II).

0.1440 g substance: 0.4480 CO_2; 0.0836 g H_2O. Found %: C 84.54; H 6.39. $C_{24}H_{22}O_2$. Calculated %: C 84.21; H 6.41. 0.1897 g substance; 15.91 g benzene: Δt 0.134°.

Found: M 440 $C_{24}H_{22}O_2$. Calculated: M 342. 0.1001 g substance: 6.1 ml C_2H_6 (17°, 754.8 mm). $C_{24}H_{21}O(OH)$. Calculated: 6.55 ml C_2H_6.

Tests for carbonyl and phenoxy groups gave negative results.

Oxidation. 0.7 g substance was dissolved in 25 ml acetone. To the solution was added 0.95 g potassium permanganate in small portions. The temperature of the reaction mass was not raised to above 30°. Slight heating occurred during the oxidation. The reaction was complete in 2 1/2 hours.

The volatile neutral products contained acetophenone (no depression of melting point of its semicarbazone in admixture with acetophenone semicarbazone). The neutral products which distilled with difficulty in steam consisted of a resin from which we were unable to isolate any pure substances.

In the acid products were detected formic acid (it reduced a solution of mercuric chloride to mercurous chloride and gave a readily decomposed silver salt) and methylphenylglycollic acid which readily broke down to acetophenone and formic acid. The decomposition products of this acid were identified. There was also isolated an acid with m.p. 130-134° which gave a red coloration with iron chloride and was readily brominated to form a debromide with m.p. 80-83°. The silver salt of this acid readily decomposed.

4) 1-Methylphenylmethylene-2-(p-hydroxyphenyl)-3-methylindene (VI).

The yellow crystalline substance isolated after precipitation of the products with m.p. 154-160° and 80-82° melted at 110-120°. The melting point rose to 125-127° after recrystallization from a mixture of ether and petroleum ether. The loss during purification was 30-40%.

The golden yellow hexagonal prisms of this compound were poorly soluble in petroleum ether, dilute alcohol and acids, highly soluble in ether, benzene, acetone, alcohol and glacial acetic acid. The absorption maximum in alcoholic solution lies at 330 mμ (Fig. 1, curve IV).

It gives a crimson coloration in concentrated sulfuric acid. With alkalis it forms phenolates difficultly soluble in organic solvents. It readily decolorizes bromine water and potassium permanganate solution. If forms a greenish-yellow solution in alcoholic alkali. The substance readily couples with diazotized p-nitroaniline.

0.1887 g substance: 0.6182 g CO_2, 0.0998 g H_2O. 0.1067 substance: 0.3324 g CO_2, 0.0548 g H_2O. Found %: C 88.44, 89.18; H 5.93, 6.04. $C_{24}H_{20}O$. Calculated %: C 83.90; H 6.22. 0.0507 g substance: 3.03 ml C_2H_6 (12°, 755.4 mm). 0.0704 g substance: 4.12 ml C_2H_6 (12°, 755.4 mm). $C_{24}H_{19}(OH)$. Calculated C_2H_6 3.6 ml, 4.86. 0.0358 g substance: 0.4305 g camphor: Δt 10.3°. Found: M 321. $C_{24}H_{20}O$. Calculated: M 324.

Oxidation. A solution of 3.6 g potassium permanganate in acetone was added to a solution of 2.8 g of the substance in 150 ml acetone. During oxidation the temperature rose to 30-40°.

Acetophenone was found in the neutral volatile portion. The neutral difficultly volatile portion was a resin from which a pure compound could not be isolated.

The acid products contained o-phthalic acid with m.p. 143-145°.

0.0196 g substance: 0.0105 g Ag. Found %: Ag 53.40. $C_8H_4O_4Ag$. Calculated %: Ag 53.00.

Acetylbenzoic acid was also found with m.p. 112-118°. 0.0119 g substance; 0.0047 Ag. Found %: Ag 39.49. $C_9H_7O_3Ag$ Calculated %: Ag 39.85.

The proposed structure is supported by a comparison of the spectral curve of the compound (Fig. 3, max. 330 mμ) with the curves of indene derivatives.

5) 2,5-Dimethyl-2,5-diphenyl-3-phenoxydihydrofuran-2,5 (V).

Vacuum fractionation yielded a viscous light-yellow oil with b.p. 230-260° at 5-10 mm. Yield 5-6 %. The product was readily soluble in benzene, ether, petroleum ether, acetone and chloroform; sparingly soluble in methyl and ethyl alcohols. It does not react with alkalis and is insoluble in these. It decolorizes bromine water and turns concentrated sulfuric acid yellow; it does not contain hydroxyl groups.

0.2030 g substance: 0.6280 g CO_2; 0.1214 g H_2O. Found %: C 84.50; H 6.60. $C_{24}H_{22}O_2$. Calculated %: C 84.21; H 6.41. 0.0370 g substance; 0.2340 g camphor: Δt 19.7°. Found: M 334. $C_{24}H_{22}O_2$. Calculated: M 342.

Determination of the phenoxy group. A mixture of 0.4 g substance with 5 ml glacial acetic acid and 8 ml hydriodic acid was heated at the boil for 10 hours. After cooling, the reaction mass was worked up with sodium thiosulfate and sodium carbonate and distilled with steam. Tribromphenol was precipitated from the condensate in admixture with a red substance. After purification the tribromphenol caused no depression in a mixed melting point test. The melting of the mixture with authentic tribromphenol was 89-91°.

Oxidation. A solution of 1.0 g potassium permanganate in 50 ml acetone was added to a solution of 2.3 g substance in 50 ml acetone.

In the neutral volatile products were found acetophenone and phenol (identified respectively as the semicarbazone and tribromphenol). In the residue, after steam distillation, was found a resinous substance (m.p. about 40°).

From the acidic products were isolated formic acid (reduces mercuric chloride solution to calomel, gives a readily decomposed silver salt and a lead salt sparingly soluble in alcohol) and methylphenylglycollic acid with m.p. 59-63°.

The aqueous solution of the acid turned brown when shaken with manganese dioxide and decolorized completely when heated. Acetophenone and formic acid were found in the decomposition products.

0.0109 g substance: 0.0043 g Ag. Found %: Ag 39.4. $C_9H_9O_3Ag$. Calculated %: Ag 39.5.

6) 1-Methylphenylmethylene-2-phenoxy-3-methylindene (X).

An amorphous yellow substance melting at about 50° was found in the flask residue after distilling off the dihydrofuran derivative. It dissolves with difficulty in alcohol, readily in ether, benzene, gasoline,

acetone and chloroform. Negative results were obtained in tests for hydroxyl and carbonyl groups. It was impossible to purify this substance completely from 2,4-dimethyl-2,5-diphenyl-3-phenoxydihydrofuran-2,5.

0.1130 g substance: 19.81 g benzene: Δt 0.088°. Found: M 344. $C_{24}H_{20}O$. Calculated: M 324. $C_{24}H_{22}O$. Calculated: M 342. 0.1553 g substance: 0.4932 g CO_2; 0.0908 g H_2O. 0.1462 g substance: 0.4674 g CO_2; 0.0860 g H_2O. Found %: C 85.45, 86.88; H 6.49, 6.49. $C_{24}H_{20}O$. Calculated %: C 88.90; H 6.20. $C_{24}H_{22}O_2$. Calculated %: C 84.21. H 6.41.

Comparison of its spectral absorption curve (maximum 330 mμ) with the curves for benzfulvene derivatives (Fig. 3) reveals a similarity of structure.

SUMMARY

1. It is shown that the reaction of both of the isomers of symm. dimethyldiphenylbutynediol with phenol in presence of sulfanilic acid proceeds in various directions with formation of no fewer than six compounds.

2. The following three condensation products are similar in structure to the products obtained from dimethylphenylbutynediol and phenol: 2,5-dimethyl-2,5-diphenyl-3-phenoxydihydrofuran-2,5; 1-methylphenylmethylene-2-(p-hydroxyphenyl)-3-methylindene; and 1-methylphenylmethylene-2-phenoxy-3-methylindene.

3. It is shown that the products of addition of phenol at the triple bond can exist in cis- and trans-forms. In the case of symm. dimethyldiphenylbutynediol the trans-form predominates among the addition products.

4. The behavior of acetylenic γ-glycols during condensation with phenol depends on the character and arrangement of the radicals at the tertiary alcoholic carbon atom. An unsymmetrical structure of the acetylenic γ-glycols facilitates the formation of the cis-form of the intermediate products. The yield of condensation products derived from the cis-form decreases with replacement of methyl groups by phenyl groups.

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Received December 30, 1950.

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THE INHIBITING ACTION OF ALDEHYDES

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The protective action of inhibitors of acidic corrosion depends on the nature of the inhibitor, its molecular weight and structure, and its concentration, as well as on the concentration of the acid, temperature, etc. Inhibitors belonging to different groups of compounds give different coefficients of inhibiting action; moreover, the coefficients of inhibiting action are observed to fluctuate within a given class of inhibitors. An important practical and theoretical problem is the correlation of this variation with the molecular weight, structure, and other factors.

It has been pointed out in a series of investigations that within a given class or group of inhibitors the inhibiting effect depends on the molecular weight of a substance in a given class. Thus, Speller and Chappell [1], Sieverts and Lueg [2] and Rhodes and Kuhn [3] investigated the speed of solution of iron, aluminum and zinc in sulfuric and hydrochloric acids containing nitrogen compounds, starting from the simplest members and finishing with alkaloids, and found that the protective action of inhibitors increases with increasing molecular weight. In addition, they found a dependence between the protective action and the molecular structure and concentration of the inhibitor. They found that the inhibiting action is increased by introducing methyl, ethyl and amino groups into the molecules of acridine, pyridine, quinoline and their derivatives. For instance the introduction of one methyl group into the pyridine molecule increases the inhibiting effect by 25%. These observations, however, are not confirmed by other investigators. In fact, Rhodes and Kuhn themselves remark that the introduction of hydroxyl groups into organic nitrogen compounds—pyridine, quinoline and acridine—causes not an increase, but a decrease of protective action. Consequently not every group introduced into a molecule of a given inhibitor causes a rise in protective action.

The molecular structure of the inhibitor also has a considerable influence on the change of rate of solution of the metal. Thus, Mann, Lauer and Hultun [4] found, in a study of the action of aliphatic amines, that secondary amines protect iron against solution in acids better than primary amines, while tertiary amines are better protectors than secondary amines. The same authors found that iso compounds have a lower inhibiting effect than normal compounds.

We have systematically investigated the inhibiting effect of aliphatic and aromatic aldehydes on acidic corrosion with the objective of determining the effect of molecular weight and structure of the aldehydes on their protective action.

Experimental procedure. We used a gravimetric method for the most part, but a volumetric method in some cases. Portevin's method was also applied to the examination of the kinetics during the initial stage of dissolution of metal in acid. Chemically pure aldehydes were utilized as inhibitors. These were formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde and enanthaldehyde (aliphatics), and benzaldehyde, cuminaldehyde and tolualdehyde (aromatics). The test objects were sheets of boiler-plate (steel 20) with dimensions of 21 x 50 x 2.5. The corrosive medium was sulfuric acid (chemically pure) in various concentrations, in the amount of 70 ml per sheet. Small beakers containing the inhibitors were placed in a thermostat an hour before an experiment in order to establish the required temperature. All experiments were performed at 25° ± 0.1° for a period of 3 hours.

Prior to an experiment, the sheets were treated by our standard method, namely, they were polished to high gloss with the appropriate grades of emery cloth, washed with alcohol and ether, brought to constant weight in a desiccator, and weighed. Following an experiment, the layer of rust was removed with water and the sheet washed with alcohol and ether before reweighing. The loss in weight was calculated as grams per square meter per hour. The inhibiting effect was calculated from the formula:

$$\gamma = \frac{\rho_0}{\rho},$$

where γ is the inhibiting effect, ρ_0 is the velocity of solution of the metal in the uninhibited acid, ρ the velocity of solution in the inhibited acid.

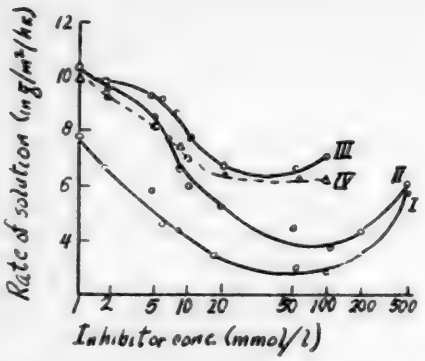

Figure 1. Dependence of rate of solution of steel in 5 N sulfuric acid on the nature and concentration of the inhibitors. I)formaldehyde; II) acetaldehyde; III) propionaldehyde; IV) butyraldehyde

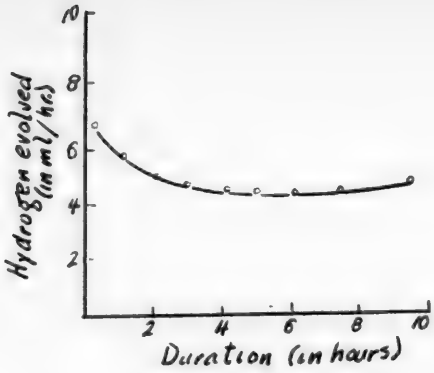

Figure 2. Rate of dissolution of steel in 5 N sulfuric acid in presence of butyraldehyde.

As mentioned above, in some cases, we also utilized a volumetric method. For this purpose we employed a cylindrical funnel fixed to a buret. Each experiment was repeated several times.

Aliphatic aldehydes. Formaldehyde and acetaldehyde were investigated in solutions containing 1 to 500 mmol/liter; propionic aldehyde and butyraldehyde in concentrations of 1 to 100 mmol/liter (due to their limited solubility). Results are presented in Table 1 and Figure 1.

TABLE 1

Inhibiting Action of Formaldehyde, Acetaldehyde, Propionaldehyde and Butyraldehyde on the Dissolution of Steel in 5 N Sulfuric Acid

Conc. of aldehydes (in mmol/l)	Speed of solution (in g/m²/hour)				Inhibiting effect			
	form-aldehyde	acet-aldehyde	propion-aldehyde	butyr-aldehyde	form-aldehyde I	acet-aldehyde II	propion-aldehyde III	butyr-aldehyde IV
0	12.24	12.24	12.24	12.24	1.00	1.00	1.00	1.00
1	7.92	10.38	10.00	10.38	1.54	1.2	1.22	1.18
2	6.94	9.81	9.65	9.15	1.76	1.25	1.27	1.34
4	5.96	8.41	9.29	8.0	2.05	1.46	1.32	1.49
6	4.92	7.88	9.01	7.90	2.49	1.55	1.36	1.55
8	4.56	6.91	8.47	7.49	2.68	1.77	1.45	1.67
10	3.87	6.12	7.79	7.13	3.17	2.00	1.57	1.72
20	3.47	5.30	6.83	6.72	3.53	2.31	1.79	1.82
50	3.10	4.45	6.66	6.48	3.95	2.75	1.48	1.89
100	2.84	3.58	7.10	6.34	4.41	3.42	1.72	1.93
200	3.44	4.48	–	–	3.55	2.73	–	–
500	5.75	5.85	–	–	2.12	2.01	–	–

We observe from Table 1 and Figure 1 that the velocity of solution of the metal (g/m²/hour) decreases with increasing concentration of formaldehyde, falls to a minimum at a concentration of 100 mmol/liter, and again starts to increase with further increase in concentration.

Concerning the inhibiting action of acetaldehyde, it might have been expected, as stated in the literature, that its protective action would surpass that of formaldehyde due to its higher molecular weight, but our data show that acetaldehyde is a weaker inhibitor than formaldehyde at all concentrations. It is interesting to note that the inhibiting action of acetaldehyde increases in the same way as that of formaldehyde but only up to a certain

concentration. The maximum of protective action of acetaldehyde occurs at the same concentration as for formaldehyde.

Coming to the next aldehyde in order of molecular weight (propionaldehyde), we find that its protective action is weaker than that of formaldehyde or acetaldehyde. At all concentrations, with exception of 100 mmol/liter, the inhibiting action of propionaldehyde increases with increasing concentration.

Consequently, above certain concentration the inhibiting action of the aldehydes is extremely weak, and at still higher concentrations the aldehydes accelerate the corrosion. Similar observations were made for the first time in respect of formaldehyde by Balezin and Novikov [5]. We propose to call that concentration of inhibitor at which limiting protective action is attained the maximum effective concentration. As our experiments showed, the maximum effective concentration is not identical for all the aldehydes. It also follows from our data that the higher the molecular weight of the aldehydes, the lower their inhibiting effect, while the higher the aldehyde concentrations after attainment of the maximum effective concentration the weaker the inhibiting action of the aldehyde.

A volumetric method was utilized for studying the velocity of solution of the metal in the inhibiting acid. We studied the rate of evolution of hydrogen by determining the time required for 5 ml of hydrogen to be released from a buret filled with a solution of the inhibited acid. The observations showed that in the case of acetaldehyde-inhibited acid, at first hydrogen was evolved rather vigorously and then the rate fell off, only to increase again after a certain period. The same phenomenon was noted with butyraldehyde, as shown in Figure 2. In the case of acetaldehyde the change in rate of dissolution after the maximum effective concentration was higher than in the case of butyraldehyde. This phenomenon was at first puzzling. We carried out a series of supplementary experiments to clarify it, studying the kinetics of solution of the metal over a period of several days in propionaldehyde-inhibited 5 N sulfuric acid at a temperature of 20°. The results showed that the rate of solution of the metal increases with passage of time regardless of the presence of inhibitor in fairly high concentrations (Table 2).

TABLE 2

Rate of Dissolution of Steel in Propionaldehyde – Inhibited Acid (Inhibitor Conc. 50 mmol/l)

Duration of expt. (in hrs)	Loss of wt. ($g/m^2/hr$)	Inhibiting effect
2	6.42	1.91
12	7.87	1.55
25.5	9.07	1.35
37.5	10.02	1.22
50.0	11.55	1.10

TABLE 3

Inhibiting Effect of Aldehydes (Volumetric Method of Investigation; Amount of Inhibitor 50 mmol/l)

Name of inhibitor	Mol. wt. of inhibitor	No. of ml H_2 released per hr	Inhibiting effect
Formaldehyde	30.02	0.66	13.96
Acetaldehyde	44.03	1.84	4.94
Propionaldehyde	58.05	3.42	2.68
Butyraldehyde	72.06	4.71	1.94
Isobutyraldehyde	72.06	3.26	2.8

The data of Table 2 show that the inhibiting effect of propionaldehyde gradually declines but not uniformly.

Investigation of the inhibiting effect of some aliphatic aldehydes by the volumetric method showed that their protective action falls off with rising molecular weight (Table 3).

These experiments show that the higher the molecular weight the lower the inhibiting effect of the aldehyde (Figure 3).

Effect of products of reduction of aldehydes on their protective action. As was shown, the protective action first increases with increasing concentration of aldehydes and subsequently begins to decrease. We have suggested that this is the consequence of reduction of the aldehydes under the action of the hydrogen evolved during dissolution of the metals in acid. Conversion of aldehydes into alcohols is a well-known reaction. The literature states that this reduction proceeds under the effect of certain catalysts and in certain conditions of the medium. For example, as far back as 1895, Kaufman [6] studied the reduction of benzaldehyde by atomic hydrogen, and Law [6] has studied the reduction of a series of aromatic aldehydes. Reduction of aldehydes to alcohols by hydrogen is also described in a number of patents.

We must, therefore, assume that also in our experiments reduction of aldehydes takes place. We therefore performed a number of experiments to determine the susceptibility of aldehydes to reduction, as a function of their molecular weight. The results are presented in Table 4.

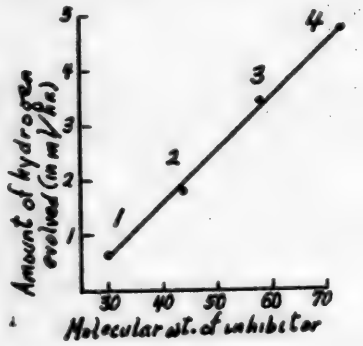

Figure 3. Dependence of rate of dissolution of steel in 5 N sulfuric acid on the molecular weight of the inhibitor.
1) formaldehyde; 2) acetaldehyde; 3) propionaldehyde; 4) butyraldehyde

TABLE 4

Susceptibility of Aldehydes to Reduction to Alcohols

Aldehyde	Amt. of hydrogen evolved (in ml)*	Vol. of hydrogen actually evolved (in ml)	Amount of hydrogen used in the reduction	
			(in ml)	(in %)
Formaldehyde	54.42	44.57	9.85	18.10
Acetaldehyde	49.20	44.66	4.54	9.25
Propionaldehyde	47.60	44.48	3.12	6.55
Butyraldehyde	46.20	44.25	1.94	4.26

The volumetric method brings out the point that with increasing concentration above the maximum inhibiting point, the velocity of dissolution increases, since the susceptibility of the aldehydes to reduction depends on their concentration in solutions. Our data for the susceptibility of aldehydes to reduction at various concentrations are presented in Table 5.

TABLE 5

Susceptibility of Aldehydes to Reduction at Various Concentrations

Conc. (in mmol/l)	Duration of expt. (hrs)	Total hydrogen formed (in ml)	Vol. of hydrogen actually evolved (in ml)	Amount of hydrogen			Inhibiting effect
				evolved per hr (in ml)	consumed in reduction (in ml)	consumed in reduction (in %)	
50	24.8	49.20	44.66	1.84	4.54	9.25	4.98
100	28.0	56.90	44.90	1.60	12.00	21.1	5.71
250	33.8	68.93	44.84	1.33	24.09	34.9	6.90
500	41.6	94.58	46.29	1.11	48.22	51.0	8.22

We see from the data of Table 5 that the volume of hydrogen collecting in the buret at certain concentrations is less than the volume of hydrogen formed in reaction between metal and acid. With increasing concentration, the difference between these volumes increases.

We see from the presented data that with rising aldehyde concentration the inhibiting effect is intensified, but side by side an opposing effect is developed, an effect which promotes solution. Above a certain concentration the protective action of the inhibitor begins to fall off because the solution-promoting effect then begins to predominate.

The reduced aldehyde promotes solution because, like any other oxidizing agent, it brings about removal of hydrogen from the surface of the metal and, consequently, makes room for release of fresh hydrogen ions, i e. it accelerates the process of solution of the metal. Hence the higher the concentration of aldehyde, the greater its oxidizing effect. At certain concentrations of aldehydes, the latter begin to lose their protective action.

Protective action, molecular weight and molecular structure of the inhibitor. On the basis of the experimental results the inhibiting action of aldehydes may be expressed by the equation:

$$\gamma = 1 + \frac{K}{M},$$

where M is the molecular weight and K a constant.

* The volumes of hydrogen are here and later converted to normal conditions.

Our results are entirely in conflict with established views on the relation between inhibiting effect and molecular weight. We have already noted that it is asserted in the publication of a series of investigators that the magnitude of the inhibiting effect increases with increasing molecular weight. Our experiments have shown that in respect to the aliphatic aldehydes the reverse relationship holds.

Other experiments were performed to clarify the relative inhibiting effects of iso and normal compounds. The substances used in these tests were butyraldehyde and isobutyraldehyde. On the basis of the literature it was to be expected that butyraldehyde would be a better inhibitor than isobutyraldehyde. In the case of amines, for instance, Mann, Lauer and Hultun found that iso compounds have a lower inhibiting power. We obtained contradictory results (Table 6).

TABLE 6

Inhibiting Effect of Butyraldehyde and Isobutyraldehyde

Conc. (mmol/l)	Speed of solution ($g/m^2/hr$)		Inhibiting effect	
	butyr-aldehyde	isobutyr-aldehyde	butyr-aldehyde	isobutyr-aldehyde
1	10.38	10.01	1.28	1.11
2	9.15	10.00	1.34	1.22
4	8.22	9.07	1.49	1.35
6	7.90	8.66	1.55	1.41
8	7.49	8.50	1.67	1.44
10	7.13	8.14	1.72	1.50

TABLE 7

Inhibiting Effect of Acetaldehyde and Benzaldehyde

Conc. of aldehydes	Speed of solution ($g/m^2/hr$)		Inhibiting effect	
	acet-aldehyde	benz-aldehyde	acet-aldehyde	benz-aldehyde
1	10.38	10.79	1.2	1.13
2	9.81	9.29	1.25	1.32
4	8.41	7.45	1.46	1.64
6	7.88	7.05	1.55	1.74
8	6.91	6.63	1.77	1.84
10	6.12	6.64	2.00	1.85

We see that butyraldehyde is a better inhibitor than isobutyraldehyde. We obtained different results in experiments using the volumetric method. Table 3 shows that the rate of evolution of hydrogen per hour is higher in presence of butyraldehyde than in presence of isobutyraldehyde The resultant calculations give a higher inhibiting effect with isobutyraldehyde than with butyraldehyde.

In our view, the divergence between the results of gravimetric and volumetric experiments can be interpreted as follows: it was previously shown that with increasing molecular weight, i.e., with lengthening of the carbon chain of the aldehydes, the inhibiting effect declines. Isobutyraldehyde has a shorter chain than normal butyraldehyde, and it is therefore natural to expect a higher inhibiting effect with the former. This is evidently associated with the fact that butyraldehyde is reduced by atomic hydrogen more readily than isobutyraldehyde.

Aromatic aldehydes. We have made a comparison of the inhibiting effects of aromatic and aliphatic aldehydes. Comparative data for acetaldehyde and benzaldehyde are given in Table 7.

TABLE 8

Inhibiting Action of Emulsions of Enanthaldehyde and Cuminaldehyde

Conc. of aldehydes (mmol/l)	Rate of solution ($g/m^2/hr$)		Inhibiting action	
	enanth-aldehyde	cumin-aldehyde	enanth-aldehyde	cumin-aldehyde
0.5	–	9.04	–	1.35
1	9.86	7.84	1.24	1.56
2	9.16	6.99	1.34	1.75
4	8.30	6.42	1.47	1.91
6	7.60	6.45	1.61	1.99
9	6.83	5.58	1.79	1.86
10	6.10	6.64	2.00	1.84

The results indicate that the rate of solution of metal is slowed down more uniformly with acetaldehyde than with benzaldehyde. With benzaldehyde, the rate of solution falls sharply as the concentration changes from 1 to 4 mmol/l and then is inhibited at an approximately uniform rate.

Inhibiting action of emulsions of aldehydes. Taking advantage of the ability of enanthaldehyde and cuminaldehyde to dissolve readily in ethyl alcohol, we dissolved definite amounts of these aldehydes in 50 ml 95% ethyl alcohol and then diluted the solutions with water to form emulsions. These were examined as inhibitors of acidic corrosion (Table 8).

We see that the rate of solution of metals in presence of enanthaldehyde falls more uniformly than in presence of cuminaldehyde.

Cuminaldehyde has a higher molecular weight than enanthaldehyde and at concentrations of 10 mmol/l it possesses a lower inhibiting effect.

The results of investigation of aldehyde emulsions thus demonstrate that not only solutions of aldehydes, but also emulsions of aldehydes exert an inhibiting action, while with the latter a characteristic feature is that the inhibiting effect falls off with rising molecular weight.

SUMMARY

1. We have refuted in the case of aldehydes the widely held belief that the inhibiting effect is intensified with increasing molecular weight.

2. It is shown that aldehydes act on the dissolution of steel in two directly opposing directions – inhibition of dissolution and acceleration thereof. At a certain magnitude of concentration, acceleration of dissolution of metal in acid begins to predominate.

3. The inhibiting action of aldehydes increases with rise of concentration only up to a determined value of the concentration. The rate of reduction of aldehydes, and consequently the accelerating effect, increases with rising concentration of the aldehyde and decreases with increasing molecular weight.

4. Emulsions of aldehydes are also shown to act as inhibitors.

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Received March 26, 1950

AROMATIC DISULFIDES AND MERCAPTANS

1. 2-MERCAPTO-4-NITROBENZOIC ACID AND ITS TRANSFORMATIONS

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In recent years p-aminosalicylic acid and its derivatives have attracted the attention of investigators owing to the high antitubercular activity of the acid. For the same reason attention is merited by p-amino-o-mercaptobenzoic acid (p-aminothiosalicylic acid) particularly since its gold-sodium salt has also been utilized for some years in tuberculosis therapy [1].

The preparation and properties of p-aminothiosalicylic acid have not been described in the literature, but have been mentioned in a series of patents [2]. It is reported, for example [2b], that 2,4-mercaptoaminobenzoic acid is prepared from 4-nitroanthranilic acid by diazotization, by the diazo reaction with potassium thiocyanate in presence of copper thiocyanate and by reduction of 2-thiocyano-4-nitrobenzoic acid. No details are given of the method of preparation and of the properties of the intermediate products, and only the melting point of 2-mercapto-4-aminobenzoic acid is given.

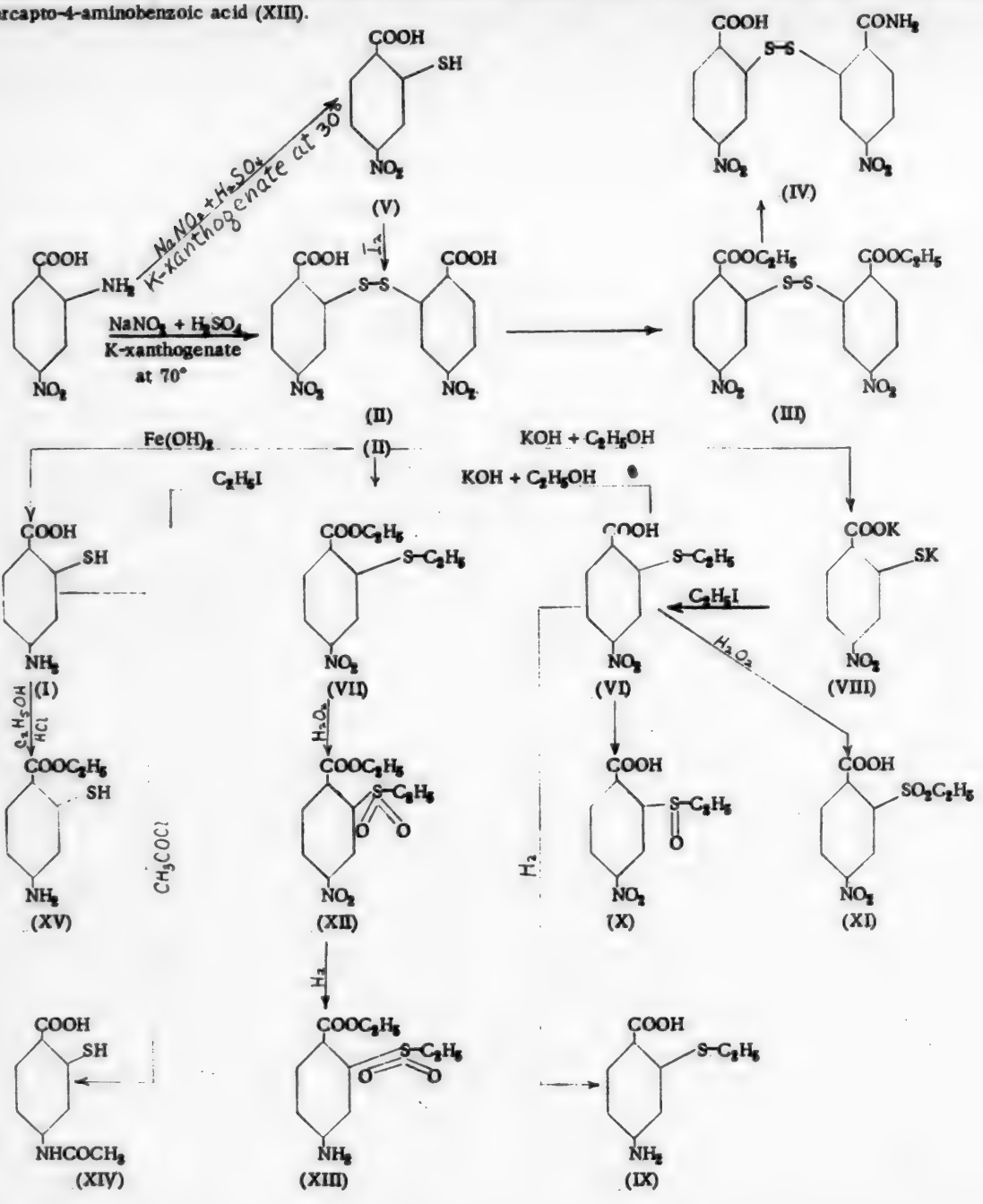
It was recently reported [3] that 2,4-mercaptoaminobenzoic acid was prepared by diazotization of 4-nitroanthranilic acid, treatment of the diazonium salt with sodium sulfide, and reduction of the resultant 2,2'-disulfide of 4-nitrobenzoic acid with the help of an iron sulfide suspension. The constants of the disulfide were not stated; the m.p. of 4-amino-2-mercaptobenzoic acid was given as 197°; that of its acetate as 137°. The last value does not agree with our own value (292°) nor with the literature value [4].

We studied the preparation of 2-mercapto-4-aminobenzoic acid (I) from 4-nitroanthranilic acid by diazotization, replacement of the diazo group by the sulfhydryl group, and reduction of the nitro group. Since decomposition of the diazonium salt with sodium sulfide solution leads to contamination with substances not easily amenable to purification, we utilized the method of treatment of the diazonium salt solution with potassium xanthogenate at 50°, followed by maintenance for 3 hours at 70° and for 24 hours at room temperature. Several authors [5] point out that in such conditions mercaptans are not formed, but the corresponding disulfides are. And indeed, the substance which we obtained had the high melting point (272-274°) characteristic of disulfides and poor solubility, and did not give the reaction for the sulfhydryl group with iron chloride in an alcoholic medium or with nascent nitrous acid [6]. The diethyl ester (III) prepared from 2,2'-dithiobis-4-nitrobenzoic acid (II) likewise did not give these reactions. By treatment with aqueous ammonia this ester gave the monoamide of 2,2'-dithiodi-4-nitrobenzoic acid (IV). On treating the diazotized p-nitroanthranilic acid, however, with potassium xanthogenate at a lower temperature for a shorter period, there is formed, in addition to the disulfide, a substance with a much lower melting point (183-185°) which is readily soluble in alcohol and glacial acetic acid, and is converted by titration with iodine into the disulfide with m.p. 270-274°. This compound, 2-mercapto-4-nitrobenzoic acid (V), is soluble in dilute caustic alkalis and ammonia with formation of the bright-red solutions characteristic of mercaptans. The corresponding disulfide gives a yellow coloration with dilute caustic alkalis. 2-Mercapto-4-nitrobenzoic acid changes into the disulfide when recrystallized from alcohol.

It is interesting to note that treatment of 2,2'-dithiobis-4-nitrobenzoic acid with ethyl iodide in alcoholic caustic alkali solution results in rupture of the disulfide bond. This reaction yields 2-ethylmercapto-4-nitrobenzoic acid (VI) and a small quantity of its ethyl ester (VII). The same acid is obtained by acting on the disulfide with diethyl sulfate and alkali. Rupture of the disulfide bond also takes place under the action of alcoholic potassium hydroxide when the dark-red crystalline potassium mercaptide of 2-mercapto-4-nitrobenzoic acid (VIII) is formed, heating of which with ethyl iodide leads to the same 2-ethylmercapto-4-nitrobenzoic acid. The latter is converted into 2-ethylmercapto-4-aminobenzoic acid (IX) by reduction with hydrogen in presence of skeletal nickel catalyst, while the corresponding sulfoxide (X) and sulfone [7] (XI) are obtained by oxidation with the calculated amount of 30% hydrogen peroxide.

Similarly the ethyl ester of 2-ethylmercapto-4-nitrobenzoic acid was converted by 30% hydrogen peroxide

into the sulfone (XII), hydrogenation of which in presence of skeletal nickel catalyst gave the ethyl ester of 2-ethylmercapto-4-aminobenzoic acid (XIII).



A more convenient method for preparation of 2-mercapto-4-aminobenzoic acid (I) proved to be the reduction of the 2,2'-disulfide of 4-nitrobenzoic acid with ferrous hydroxide [8]. The acid obtained in 65% of the theoretical yield gives a definite reaction for the presence of a sulfhydryl group. It melts at 197-198° and forms salts both with bases and with acids, but the latter are very easily hydrolyzed so that the acid can be recovered from an ammoniacal solution of its salt by acidification with hydrochloric acid. Its hydrochloride cannot be recrystallized even from absolute alcohol.

2-Mercapto-4-aminobenzoic acid reacts with bases, to form salts, both at the carboxyl and at the sulfhydryl group. It titrates with two equivalents of alkali.

Reaction of 2-mercapto-4-aminobenzoic acid with an equimolecular amount of acetyl chloride in presence of pyridine gives 4-acetamino-2-mercaptobenzoic acid (XIV). The ethyl ester of 2-mercapto-4-aminobenzoic acid (XV) is formed by esterification with ethyl alcohol in presence of hydrogen chloride.

The reactions carried out in this investigation are summarized in the above scheme.

EXPERIMENTAL

1. 2,2'-Dithiodi-4-nitrobenzoic acid (II) To a mixture of 12 g 4-nitroanthranilic acid and 30 ml water is added dropwise with cooling and stirring 14.5 ml concentrated sulfuric acid. The mixture is then cooled to +2° and dropwise addition is made of a solution of 7.8 g sodium nitrite in 11 ml water. After keeping for an hour, the reaction mixture is added with energetic stirring to a solution of 12 g potassium xanthogenate and 45 g sodium carbonate in 400 ml water heated to 50°. The temperature of the cherry-red solution is then raised to 70° and held there for 3 hours and then at room temperature for 24 hours. The yellow crystalline precipitate is filtered off, dissolved in a little water, filtered, and again precipitated, as a light-yellow mass, by means of concentrated hydrochloric acid. The precipitate is filtered, washed with water and dried to give 5.8 g of material melting with decomp. at 268-275°. After recrystallization, first from glacial acetic acid and then from acetone, 2,2'-dithiodi-4-nitrobenzoic acid is obtained in the form of light-yellow, fine crystals with m.p. 272-274°. The acid is readily soluble in acetone, soluble in hot alcohol, glacial acetic acid and dioxan, insoluble in water, ether, petroleum ether, benzene, chloroform and carbon tetrachloride; it dissolves very readily in bicarbonate solution and dilute caustic alkalis to form light-yellow solutions. It dissolves in strong caustic alkalis with a dark-cherry coloration. Its ammonium, sodium and potassium salts crystallize in large, light-yellow needles which are soluble in water. It does not give a positive reaction for the sulfhydryl group either with iron chloride in alcohol or with sodium nitrite in glacial acetic acid; it does not decolorize 0.1 N iodine solution.

3.300 mg substance: 5.125 mg CO_2; 0.721 mg H_2O. 6.100 mg substance; 0.387 ml N_2 (23.5°, 738.0 mm). 5.351 mg substance: 6.070 mg $BaSO_4$. Found %: C 42.36; H 2.44; N 7.09; S 15.57. $C_{14}H_8O_8N_2S_2$. Calculated %: C 42.4; H 2.03; N 7.07; S 16.18.

After the precipitate had been separated from the reaction mixture, the filtrate was treated with concentrated hydrochloric acid to bring down an additional 3.9 g of 2,2'-dithiodi-4-nitrobenzoic acid with m.p. 230-235° which after two recrystallizations from glacial acetic acid gave the pure acid with m.p. 272-274°.

2. Diethyl ester of 2,2'-dithiodi-4-nitrobenzoic acid (III). A mixture of 2.4 g 2,2'-dithiodi-4-nitrobenzoic acid, 1 ml concentrated sulfuric acid and 24 ml absolute ethyl alcohol is heated at the boil for 20 hours. The crystalline precipitate is filtered, well washed with water, dried and recrystallized from glacial acetic acid. Yield 1.2 g of light-yellow needles with m.p. 177°. After a second recrystallization from glacial acetic acid the diethyl ester of 2,2'-dithiodi-4-nitrobenzoic acid has m.p. 178-179°. It does not give the sulfhydryl reaction with iron chloride and sodium nitrite, and it does not decolorize iodine solution. It is readily soluble in acetone and dioxan, soluble in hot glacial acetic acid and hot alcohol, insoluble in benzene, chloroform, water and bicarbonate solution.

6.485 mg substance: 0.361 ml N_2 (24°, 726 mm). Found %: N 6.13. $C_{18}H_{16}O_8N_2S_2$. Calculated %: N 6.19.

3. 2,2'-Dithiodi-4-nitrobenzoic acid monoamide (IV). 2 g of diethyl ester of 2,2'-dithiodi-4-nitrobenzoic acid is heated with 20 ml 25% aqueous ammonia in a sealed tube at 100° for 20 hours. The solution is filtered from the small precipitate and treated with dilute hydrochloric acid to bring down 1.25 g of dark-yellow precipitate. After four recrystallizations from glacial acetic acid, the monoamide of 2,2'-dithiodi-4-nitrobenzoic acid is obtained as a light-yellow substance with m.p. 278-280°, soluble in bicarbonate, alcohol, acetone and dilute acetic acid, insoluble in water and ether.

3.605 mg substance: 0.339 ml N_2 (19.5°, 736 mm). Found %: N 10.63. 4.837 mg substance: 3.74 ml 0.01 N H_2SO_4. Found %: N 10.82. $C_{14}H_9O_7N_3S_2$. Calculated %: N 10.63.

4. 2-Mercapto-4-aminobenzoic acid (I). 12 g anhydrous iron chloride is dissolved with heating in 100 ml water and ferrous hydroxide is precipitated with 25% aqueous ammonia solution. Gradual addition is then made of a hot solution of 2.2 g 2,2'-dithiodi-4-nitrobenzoic acid in 50 ml 25% aqueous ammonia. The dark-green precipitate

of ferric hydroxide. The mixture is kept for 15 minutes on the boiling water bath; it is then filtered and the precipitate thoroughly washed with hot water. The filtrate is evaporated to half of its original volume, cooled, and treated with glacial acetic acid to bring down a cream-colored precipitate of 2-mercapto-4-aminobenzoic acid. The precipitate is filtered, washed with water and dried. Yield 1.2 g. M.p., after two recrystallizations from glacial acetic acid, 197.5-198°. Readily soluble in bicarbonate and dilute caustic alkalis; soluble in acetone, dioxan, hot dilute alcohol and hot dilute acetic acid; insoluble in benzene, chloroform and cold water. The acid gives the sulfhydryl reaction with iron chloride in alcohol and with sodium nitrite in glacial acetic acid; it at once decolorizes 0.1 N iodine solution.

3.872 mg substance: 7.091 mg CO_2; 1.443 mg H_2O. 6.425 mg substance: 0.480 ml N_2 (24.5°, 737 mm). 4.862 mg substance: 6.553 mg $BaSO_4$. Found %: C 49.95; H 4.17; N 8.30; S 18.50. $C_7H_7O_2NS$. Calculated %: C 49.67; H 4.17; N 8.28; S 18.9. 0.1115 g substance: 13.32 ml 0.1 N NaOH. Found equivalent 83.7. Calculated equivalent 84.56.

2-Mercapto-4-aminobenzoic acid gives water-soluble ammonium, sodium and potassium salts; with silver, mercury and lead cations it forms water-insoluble precipitates. On passing an excess of dry hydrogen chloride into an alcoholic solution of 2-mercapto-4-aminobenzoic acid, there is formed a white precipitate of the hydrochloride, readily soluble in alcohol and water, insoluble in concentrated hydrochloric acid; m.p. 216-220°. It could not be recrystallized because it decomposes in water or alcohol or even in absolute alcohol with separation of the original 2-mercapto-4-aminobenzoic acid.

The picrate is prepared by mixing an alcoholic solution of 2-mercapto-4-aminobenzoic acid with a hot alcoholic solution of the calculated amount of picric acid. The picrate does not come down on cooling; it is therefore separated with a large quantity of ether. It is obtained as fine, light-yellow crystals with m.p. 216°.

5. Ethyl ester of 2-mercapto-4-aminobenzoic acid (XV). 1 g 2-mercapto-4-aminobenzoic acid is dissolved in 50 ml absolute alcohol and dry hydrogen chloride is passed through until the weight increase is 0.23 g (1.1 mole). The solution is refluxed for 6 hours, evaporated to dryness in vacuum and treated with saturated bicarbonate solution. The precipitate is filtered and washed with water. Yield 0.52 g. After two recrystallizations from alcohol (1 : 1) the m.p. of the ethyl ester of 2-mercapto-4-aminobenzoic acid was 198°. Soluble in acetone, glacial acetic acid, and hot dilute alcohol; insoluble in benzene, petroleum ether, water and bicarbonate solution. Gives a positive sulfhydryl reaction with iron chloride and sodium nitrite.

6.790 mg substance: 0.428 ml N_2 (24°, 726 mm). Found %: N 6.92. $C_9H_{11}O_2NS$. Calculated %: N 7.10.

6. 2-Mercapto-4-acetaminobenzoic acid (XIV). 1 g 2-mercapto-4-aminobenzoic acid in 4 ml pyridine and 0.5 ml acetyl chloride are heated at the boil for two hours, after which the pyridine is distilled off and the residue treated with saturated sodium bicarbonate solution. The solution is filtered and treated with concentrated hydrochloric acid to precipitate 0.7 g 2-mercapto-4-acetaminobenzoic acid, a dark-yellow substance with m.p. 280-283°. After two recrystallizations from glacial acetic acid and one from alcohol the m.p. was 298-299°. It gives the sulfhydryl reaction with iron chloride. Soluble in dilute caustic alkalis, in alcohol, acetone and glacial acetic acid; insoluble in water, ether and benzene.

3.936 mg substance: 7.310 mg CO_2; 1.516 mg H_2O. 6.455 mg substance: 2.94 ml 0.01 N H_2SO_4. Found %: C 50.65; H 4.30; N 6.40. $C_9H_9O_2NS$. Calculated %: C 51.14; H 4.29; N 6.63.

7. 2-Ethylmercapto-4-nitrobenzoic acid (VI). To a cherry-red solution of 5 g 2,2'-dithiodi-4-nitrobenzoic acid in 6 ml 20% sodium hydroxide solution is added dropwise with energetic stirring 2 ml diethyl sulfate. At first the solution does not change color, but a precipitate gradually comes down and the solution acquires a light color. After heating for 5 hours on the boiling water bath, the mixture is cooled and treated with 10% sodium hydroxide solution. A small amount of insoluble material is separated by filtration and from the filtrate with the help of concentrated hydrochloric acid is precipitated a yellow substance which is filtered at the pump, well washed with water and dried. Yield 2.5 g 2-ethylmercapto-4-nitrobenzoic acid with m.p. 202-204°. After two recrystallizations from ethyl alcohol, the m.p. rose to 210-212°. The acid is soluble in acetone, hot alcohol, glacial acetic acid and dioxan; insoluble in water, chloroform and benzene.

3.492 mg substance: 6.117 mg CO_2; 1.304 mg H_2O. 5.585 mg substance: 0.315 ml N_2 (24°, 736 mm). 5.316 mg substance: 5.527 mg $BaSO_4$. Found %: C 47.77; H 4.17; N 6.28; S 14.27. $C_9H_9O_4NS$. Calculated %: C 47.54; H 3.99; N 6.17; S 14.12.

The same substance may be prepared from 2,2'-dithiodi-4-nitrobenzoic acid and ethyl iodide in alcohol alkali solution. To a solution of 5 g 2,2'-dithiodi-4-nitrobenzoic acid in 120 ml alcohol is added with stirring a solution of 2.8 g potassium hydroxide in 20 ml alcohol, then 4 g ethyl iodide, and the mixture boiled with good stirring for 9 hours. After cooling, 0.9 g of the original disulfide is recovered and the solution is evaporated to dryness and treated with bicarbonate solution. The bicarbonate-insoluble ethyl ester of 2-ethylmercapto-4-nitrobenzoic acid is separated, well washed with water and dried. Yield 0.6 g. After two recrystallizations from glacial acetic acid the m.p. is 80-81°. It does not give the sulfhydryl reaction with iron chloride. Readily soluble in alcohol, acetone, acetic acid; insoluble in water and bicarbonate.

6.200 mg substance: 0.308 ml N_2 (24.5°, 744 mm). Found %: N 5.58. $C_{11}H_{13}O_4NS$. Calculated %: N 5.49.

The remaining bicarbonate solution is acidified with hydrochloric acid to give a yellow precipitate which is filtered, well washed with water and dried. Yield of 2-ethylmercapto-4-nitrobenzoic acid 2.7 g. M.p. (from alcohol) 210-211°.

8. Reaction of 2,2'-dithiodi-4-nitrobenzoic acid with alcoholic potassium hydroxide. To a hot solution of 1.5 g 2,2'-dithiodi-4-nitrobenzoic acid in 100 ml alcohol is added a hot alcoholic solution of 2.1 g potassium hydroxide. The solution slowly reddens and on further boiling a dark-red, crystalline precipitate comes down. After heating for an hour, the precipitate is filtered, washed thoroughly with alcohol and ether. Yield 1.6 g of the potassium salt of 2-potassio-mercapto-4-nitrobenzoic acid. The mercaptide is highly soluble in water, sparingly soluble in alcohol, insoluble in ether. It could not be recrystallized. It crystallizes with one molecule of water which is lost in a vacuum desiccator at 100°.

0.2303 g substance: 0.0138 g H_2O. 3.121 mg substance: 3.240 mg CO_2; 0.548 mg H_2O. 7.900 mg substance: 0.340 ml N_2 (18.5°, 730 mm). Found %: C 28.31; H 1.36; N 4.85; H_2O 6.14. $C_7H_3O_4NSK_2 \cdot H_2O$. Calculated %: C 28.63; H 1.68; N 4.77; H_2O 5.97.

The potassium salt of 2-potassio-mercapto-4-nitrobenzoic acid is converted by boiling with ethyl iodide into 2-ethylmercaptobenzoic acid. Boiling is carried out for 30 minutes with alcohol and ethyl iodide, the insoluble residue is filtered off, and the filtrate evaporated to dryness in vacuum. The yellow residue, m.p. 220-230°, is recrystallized from glacial acetic acid and then has m.p. 208-210°. It does not depress the melting point of 2-ethylmercapto-4-nitrobenzoic acid.

9. 2-Ethylmercapto-4-aminobenzoic acid (IX). 0.8 g 2-ethylmercapto-4-nitrobenzoic acid in 50 ml alcohol is hydrogenated in presence of 2.0 g skeletal nickel catalyst at room temperature. The reaction is completed in 30 minutes. The solution is filtered, evaporated to dryness, and the residue treated with water. The white powder is separated. After two recrystallizations from glacial acetic acid, the melting point of the 2-ethylmercapto-4-aminobenzoic acid is 145.5-146°.

4.050 mg substance: 8.180 mg CO_2; 2.037 mg H_2O. 4.500 mg substance: 0.278 ml N_2 (19°, 732 mm). Found %: C 55.08; H 5.62; N 7.05. $C_9H_{11}O_2NS$. Calculated %: C 54.77; H 5.62; N 7.10.

10. 2-Ethylsulfoxide of 4-nitrobenzoic acid (X). To a solution of 1 g 2-ethylmercapto-4-nitrobenzoic acid in 50 ml glacial acetic acid is added 0.55 ml 27% hydrogen peroxide; long needles of the original acid separate out. After standing for 48 hours at room temperature the acicular crystals dissolve completely and the solution is evaporated to dryness in vacuum. Yield 1 g of the sulfoxide. After three recrystallizations alternately from 50% acetic acid and dilute alcohol, light-yellow crystals are obtained with m.p. 180-181°. 2-Ethylsulfoxido-4-nitrobenzoic acid dissolves readily in alcohol, acetone, glacial acetic acid and dioxan; sparingly in hot water, and not at all in ether.

6.985 mg substance: 0.344 ml N_2 (23.5°, 733 mm). Found %: N 5.56. $C_9H_9O_5NS$. Calculated %: N 5.76.

11. 2-Ethylsulfonyl-4-nitrobenzoic acid (XI). To a solution of 1 g 4-nitro-2-ethylmercaptobenzoic acid in 50 ml glacial acetic acid is added 1.6 ml 27% hydrogen peroxide (2.5 mole). At the end of two days the separated crystals of the original acid disappear and the solution is evaporated to dryness in vacuum. The slightly cream-colored sulfone is twice recrystallized from water in presence of carbon and then from glacial acetic acid. M.p. 191-192°. Very soluble in alcohol and glacial acetic acid, soluble in hot water, insoluble in cold water and ether.

3.813 mg substance: 5.871 mg CO_2; 1.096 mg H_2O. 8.471 mg substance: 0.385 ml N_2 (18.5°, 746 mm). Found %: C 41.99; H 3.22; N 5.11. $C_9H_9O_6NS$. Calculated %: C 41.67; H 3.50; N 5.45.

12. Ethyl ester of 2-ethylsulfonyl-4-nitrobenzoic acid(XII). To a solution of 0.82 g ethyl ester of 2-ethylmercapto-4-nitrobenzoic acid in 15 ml glacial acetic acid is added 1.5 ml 27% hydrogen peroxide. At the end of two days, the transparent solution is evaporated to dryness in vacuum. The white residue is recrystallized alternately from dilute acetic acid and alcohol. M.p. 105-107°. Very soluble in alcohol, glacial acetic acid and acetone; insoluble in hot and cold water.

4.689 mg substance: 7.830 mg CO_2; 1.949 mg H_2O. 7.497 mg substance: 0.323 ml N_2 (19°, 726 mm). Found %: C 45.54; H 4.65, N 4.81. $C_{11}H_{13}O_6NS$. Calculated %: C 45.98; H 4.59; N 4.86.

13. Ethyl ester of 2-ethylsulfonyl-4-aminobenzoic acid (XIII). 0.5 g ester of 2-ethylmercapto-4-nitrobenzoic acid in 20 ml alcohol is hydrogenated in presence of 1.0 g skeletal nickel catalyst at room temperature. The reaction is completed in one hour. The solution is filtered and evaporated to dryness and the residue recrystallized three times alternately from alcohol and glacial acetic acid. M.p. 164-165°. Fine white crystals, readily soluble in alcohol, glacial acetic acid and acetone; insoluble in water.

3.909 mg substance: 7.414 mg CO_2; 2.108 mg H_2O. 8.199 mg substance: 0.400 ml N_2 (21°, 729 mm). Found %: C 51.73; H 6.03; N 5.44. $C_{11}H_{13}O_4NS$. Calculated %: C 51.34; H 5.87; N 5.44.

SUMMARY

1. Diazotization of p-nitroanthranilic acid followed by treatment with potassium xanthogenate gave, depending on the temperature conditions, 2-mercapto-4-nitrobenzoic acid or its disulfide.

2. A study was made of the cleavage of 2,2'-dithio-bis-4-nitrobenzoic acid (disulfide) with alcoholic caustic alkali, its alkylation and esterification, and the action of ammonia on the ester.

3. 2-Ethylmercapto-4-nitrobenzoic acid and its ethyl ester were oxidized to the corresponding sulfoxide and sulfone.

4. 2-Ethylmercapto-4-aminobenzoic acid and the ethyl ester of 2-ethylsulfone-4-nitrobenzoic acid were prepared.

5. Reduction of 2,2'-dithio-bis-4-nitrobenzoic acid with ferrous hydroxide gave 2-mercapto-4-aminobenzoic acid, which was converted into the N-acetyl derivative and the ester.

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Received April 28, 1951

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ARYLSULFIDYL QUINONEIMINES*

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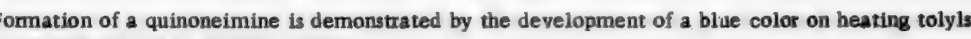
In previous papers we studied some substituted quinoneimines, namely: quinonebromimides [1,2], quinonediimides [3], and N-arylsulfonyl quinoneimines [4]. We showed that in the latter compounds the arylsulfonyl residue is split off in the form of an anion of an arylsulfonic acid under the action of alkaline solutions of phenols. In view of the importance of a study of the substitution reactions of quinoneimines, we decided also to investigate the compounds containing an arylsulfidyl radical.

(I).

Two representatives of this group of compounds – N-(4-chloro-2-nitrophenylsulfidyl)-1,4-benzoquinoneimine [5] and N-(4-tolylsulfidyl)-1,4-benzoquinoneimine [9] – are described in the literature; the authors in question, however, did not investigate their reactions with phenols. We have therefore repeated the synthesis of the first of these compounds and have studied its reaction with alkaline solutions of phenol and 1-naphthol. It transpired that the first compound only gives a blue coloration when heated in alcoholic alkali solution, i.e. it forms indophenols. Furthermore we synthesized N-(2,4-dinitrophenylsulfidyl)-1,4-benzoquinoneimine.

We synthesized arylsulfidyl quinoneimines in accordance with the scheme:

Attempts to repeat the synthesis of N-(4-tolylsulfidyl)-1,4-benzoquinoneimine [9] were unsuccessful; reaction of tolylsulfide chloride with 1,4-aminophenol in anhydrous ether gave the corresponding 4-(tolylsulfidylamino)-phenol, but this compound was unexpectedly very unstable and broke down to ditolyldisulfide and other unidentified products during crystallization. In moist ether the reaction of tolylsulfidyl chloride with 1,4-aminophenol led directly to ditolyldisulfide, i.e. 1,4-aminophenol only had, so to speak, a reducing effect on tolylsulfide chloride. The formation of ditolyldisulfide most probably takes place via the decomposition of 4-(tolylsulfidylamino)-phenol according to the equation:



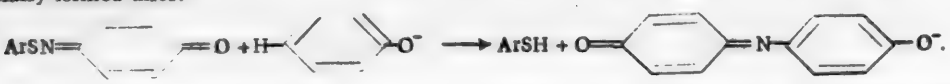
Formation of a quinoneimine is demonstrated by the development of a blue color on heating tolylsulfidylaminophenol with phenol in alkaline solution.

The (2,4-dinitrophenylsulfidyl)-1,4-benzoquinineimine, synthesized by us for the first time, like its known analog N-(4-chloro-2-nitrophenylsulfidyl)-1,4-benzoquinoneimine, had a yellow color and was fairly stable to heating; it melts without appreciable decomposition at a high temperature. Interest is attached to the action of phenol in alcoholic alkaline solution on these compounds. On heating there is developed an intense blue color or a correspondingly blended (yellow + blue) greenish-blue color due, it must be assumed, to formation of indophenol. The coloration was not observed in the cold in ammoniacal solution. With 1-naphthol in the same conditions a blue color is obtained; it must be pointed out that quinonechlorimide and quinonebromimide only give a violet coloration with 1-naphthol in an ammoniacal medium; in a medium of NaOH a blue color is developed. The violet stain formed with 1-naphthol when carrying out the quinonebromimide reaction becomes blue when moistened with 1 M caustic alkali.

We made a close examination of the action of N-(4-chloro-2-nitrophenylsulfidyl)-1,4-benzoquinoneimine on phenol in alcoholic alkaline solution; a product insoluble in the dilute alkali-alcohol solution was identified as

* The ArS radical is encountered in the literature under various names such as "arylthio" and "arylsulfid(yl)". Some substituted radicals, however (chlorides, amides, anilides, etc), are regarded as derivatives of an aryl sulfonic acid ArSOH; In conformity with this, the ArS radical is named "arylsulfen(yl)". But this name does not correspond to the composition of the radical, and we have adopted the consistent name "arylsulfidyl".

4,4'-dichloro-2,2'-dinitrodiphenyldisulfide. It appears probable that this compound is formed by oxidation of the initially formed thiol:



We know, of course, that thiophenols in alkaline solution are very rapidly oxidized to disulfides. This mechanism is supported by the fact that the isolated product at first has a low melting point and only acquires the melting point of the disulfide after keeping in the air.

Our observations have thus revealed the cleavage of the arylsulfidyl radical from arylsulfidyl quinoneimines; this fact is interesting both for characterization and identification of arylsulfidyl quininechlorimines and for our understanding of the relation between structure and properties of the radical and its ability to split off in the form of an ion from the substituted quinoneimine. We also synthesized 4-(4'-chloro-2'-nitrophenylsulfidyl)-aminoanisole and oxidized it with bichromate in glacial acetic acid. It was found that during oxidation with bichromate in glacial acetic acid, the latter combines to form a product identical with N-(4-chloro-2-nitrophenylsulfidyl)-1,4-benzoquinoneimine; evidence has consequently been obtained of cleavage of a methyl group during oxidation.

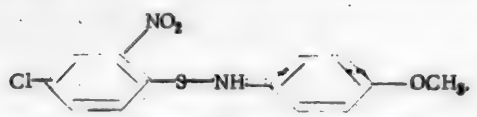
EXPERIMENTAL

The 4-chloro-2-nitrophenylsulfidyl chloride and 2,4-dinitrophenylsulfidyl chloride required for the experiments were prepared from the disulfides by the action of chlorine on a suspension in carbon tetrachloride [6].

N-(4-Chloro-2-nitrophenylsulfidyl)-1,4-benzoquinoneimine was synthesized by oxidation of 4-(4'-chloro-2'-nitrophenylsulfidylamino)-phenol [5]. The product after recrystallization from glacial acetic acid was in the form of small yellow needles melting at 194° in agreement with the literature.

No coloration is developed in the cold with phenol in alcoholic alkaline solution, but a deep blue color appears on heating. Simultaneously a yellow precipitate is formed whose amount increases when the solution is kept. The precipitate was filtered, washed and dried; m.p. 212°. The m.p. of 4,4'-dichloro-2,2'-dinitrodiphenyldisulfide is given as 212° [5].

4-(4'-Chloro-2'-nitrophenyl sulfidylamino)-anisole

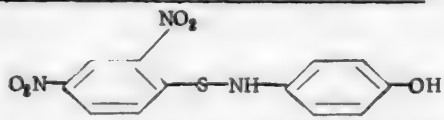


Into a solution of 10 g 4-chloro-2-nitrophenylsulfide-chloride in 150 ml absolute dry ether is introduced 10 g p-anisidine. The precipitate of p-anisidine hydrochloride is filtered off and the ethereal filtrate cooled to −15° when red crystals came out. After crystallization from glacial acetic acid the product melted at 127-128°. Sparingly soluble in benzene, insoluble in water, readily soluble in ether.

0.2156 g substance: 0.1580 g $BaSO_4$. Found %: S 10.07. $C_{13}H_{11}O_3N_2ClS$. Calculated %: S 10.32.

5 g of 4-(4'-chloro-2'-nitrophenylsulfidylamino)-anisole was dissolved in glacial acetic acid and addition was made of a concentrated solution of 5 g sodium bichromate in glacial acetic acid. The mixture was heated to the boil and allowed to stand. Next morning the yellow needlets were filtered and recrystallized from glacial acetic acid. M.p. 194°. A blue coloration appeared when heated with phenol in alkaline solution. It did not depress the melting point of the sulfidyl quinoneimine. It was thus established that oxidation of the corresponding methoxy derivative is accompanied by loss of the methyl group with formation of the sulfide-quinoneimine.

4-(2',4'-Dinitrophenylsulfidylamino)-phenol

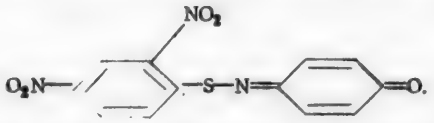


10 g 2,4-Dinitrophenylsulfidyl-chloride is dissolved in 150 ml ether, and 10 g p-aminophenol is added to the solution. The suspension of aminophenol in ether is boiled for an hour under a reflux condenser. The precipitate of

unreacted aminophenol and the aminophenol hydrochloride are filtered off and the ethereal solution cooled to −15°. The separated red crystals are filtered off and recrystallized from glacial acetic acid. Red leaflets, m.p. 155-156°, readily soluble in ether, sparingly in alcohol.

0.0980 g substance: 0.0788 g $BaSO_4$. Found %: S 11.0. $C_{12}H_9O_5N_3S$. Calculated %: S 10.4.

N-(2,4-Dinitrophenylsulfidyl)-1,4-benzoquinoneimine



Oxidation of the preceding compound was effected with bichromate in glacial acetic acid in similar conditions. Yellow needles were obtained which dissolved readily in ether and less easily in benzene and were insoluble in water. Two recrystallizations from glacial acetic acid gave yellow leaflets with m.p. 197-198°. A blue color appeared when heated with alkaline solutions of phenol and 1-naphthol. A yellow precipitate came down at the same time.

0.0874 g substance: 0.0710 g $BaSO_4$. Found %: S 10.2. $C_{12}H_7O_5N_3S$. Calculated %: S 10.5.

4-(4'-Tolylsulfidylamino)-phenol is similarly prepared from 4-tolylsulfidylchloride and 4-aminophenol in ethereal suspension. Red crystals with m.p. 68° come down from the ethereal solution. The literature gives m.p. 68° [9]. A blue color is formed when heated with phenol in alcoholic alkaline solution.

Hydrolysis occurs in aqueous alcohol. Two crystallizations from dilute alcohol give a colorless, odorless substance with m.p. 40°. It does not contain nitrogen and is insoluble in water and caustic alkali solutions. When the synthesis is performed in moist ether a colorless substance with m.p. 48° is obtained directly. A deep-violet color is developed on gentle heating in conc. sulfuric acid. Qualitative reactions identify it as ditolyldisulfide, m.p. 48° [7]. Oxidation of noncrystallizing tolylsulfidylaminophenol as well as of the colorless substance with m.p. 40° gives a colorless substance with m.p. 76°. The literature gives 78° as the melting point of ditolylsulfonedisulfide, $CH_3C_6H_4SO_2SC_6H_4CH_3$ [8]. It has therefore been demonstrated that the hydrolysis of tolylsulfidylaminophenol leads to ditolyldisulfide.

SUMMARY

1. N-(2,4-dinitrophenylsulfidyl)-1,4-benzoquinoneimine has been synthesized and its properties and reactions described.

2. Arylsulfidyldiquinoneimines give a blue coloration with phenol in alkaline solution; at the same time the arylsulfidyl residue is detached and the corresponding disulfide is formed.

3. In attempts to synthesize N-(4'-tolylsulfidyl)-1,4-benzoquinoneimine, it was established that tolylsulfidylaminophenol easily splits up with formation of ditolyldisulfide.

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Received May 22, 1951

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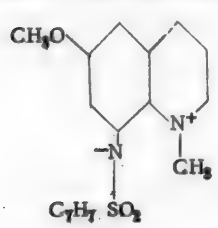
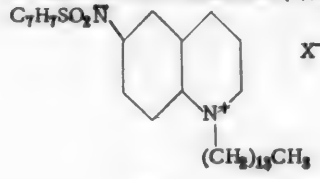
BIPOLAR IONS FORMED DURING CLEAVAGE OF A PROTON FROM THE NH GROUP. VI.

A. M. Simonov

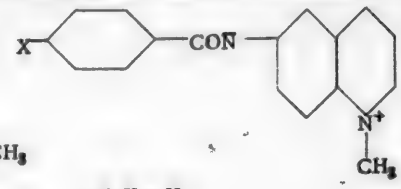
It was shown in the preceding communications that quaternary ammonium salts containing a NH group attached to a 2,4-dinitrophenyl, picryl or arylsulfonyl radical can be converted, directly or via intermediate formation of a base, into characteristic bipolar ions (betainazeniates) [1]. The formation of a negative pole in the molecules of these compounds is caused by loss of a proton from the NH group. The influence of electron-accepting groups bound to the negatively charged N atom causes a fall in the electronic density at this atom. With the aim of further investigation of the conditions of formation and the properties of bipolar ions of this type, we have synthesized the compounds with structures (I) to (III) described in this communication:



(I)



(II)



a) X = H
b) X = NO_2

(III)

In the bipolar ion of (I) the onium N atom is in the o-position (position 8) to the azeniate atom of nitrogen; in this way the compound is distinguished from the previously described betaines of this type, belonging to the series of p- and m-derivatives. The bipolar ion of (II) is characterized by the presence of a high-molecular alkyl attached to the onium N atom. A feature of the structure of the bipolar ions of (III a) and (III b) is the presence of, respectively, a benzoyl and a p-nitrobenzoyl group attached to the azeniate nitrogen atom; notwithstanding the lower electron-accepting ability of these groups in comparison, say, with the p-tolylsulfonyl radical, these groups have been found experimentally to exhibit a sufficiently high mobility of the hydrogen at the NH group to form a betaine.

Compound (I) is easily prepared by dehydration of the base isolated from the corresponding quinoline salt by treatment with ammonia. A similar method is applied to the preparation of the bipolar ions (III a) and (III b); separation of the bases from the salts in this case, however, is only possible when using a considerable excess of caustic alkali. In contrast to these compounds, the bipolar ion of (II) is formed directly from the quinolinium salt by the action of ammonia or sodium hydroxide on its aqueous alcoholic solution; this effect is evidently due to the hydrophobic character of the alkyl group, since the preparation of the related methylbetaine is only possible through intermediate formation of the base.

The prepared bipolar ions possess the same properties as the previously investigated compounds of this type. They are deeply colored crystalline substances with rather high melting points, in most cases insoluble in nonpolar solvents. Only the bipolar ion of (I) is slightly soluble in dioxan; this enables the determination of its dipole moment. Compound (II) has an extremely low solubility in dioxan in spite of the presence of the high-molecular alkyl.

EXPERIMENTAL

1. 6-Methoxy-8-(p-tolylsulfonamido)-quinoline. To a solution of 5.25 g 6-methoxy-8-aminoquinoline in 25 ml pyridine bases (b.p. 120-140°) is added 5.7 g p-toluenesulfochloride in small portions, and the reaction mixture is heated at 80-90° for $\frac{1}{2}$ hour. On the following day the crystallized mass is transferred into 250 ml hot water and the residue is filtered off and washed with water. Yield 9.2 g. It is crystallized from alcohol, benzene, and again from alcohol. White crystals with m.p. 134-135°. The literature gives 131-132° [2].

Found %: S 9.56, 9.53. $C_{17}H_{16}O_3N_2S$. Calculated %: S 9.76.

The methyl-methosulfate of 6-methoxy-8-(p-tolylsulfonamido)-quinoline was prepared by heating 6-methoxy-8-(p-tolylsulfonamido)-quinoline with a small excess of freshly vacuum-distilled dimethylsulfate. The reaction was carried out for 3 hours at 105-110° (rise of temperature to 140° causes partial decomposition, and a vitreous melt is

formed on cooling). Unreacted starting materials are washed out with boiling absolute benzene. The yield reaches 93%. White acicular crystals (from absolute alcohol), decomposing at 242-245°, very sparingly soluble in water, insoluble in acetone. When an aqueous suspension of the salt, made alkaline with potassium carbonate solution, is shaken with chloroform, the chloroform layer acquires a wine-red color due to the betaine formed.

2. Methylbetaine of 6-methoxy-8-(p-tolylsulfonamido)-quinoline (I)*. 4.0 g methyl-methosulfate of 6-methoxy-8-(p-tolylsulfonamido)-quinoline is placed in a conical flask and triturated with a rod with 20 ml 5% aqueous ammonia. A viscous red mass is formed. The aqueous solution is poured off and the viscous product is washed several times with dilute aqueous ammonia (kneading the mass with a rod). The product gradually crystallizes. It is dissolved with heating in a mixture of 25 ml alcohol and 10 ml water, filtered hot, and then 10 ml water is added. The resultant crystalline precipitate is filtered, washed with dilute alcohol and dried in a desiccator over sodium hydroxide. Yield 2.32 g. The product is twice recrystallized from 50% alcohol. The hot solution at first deposits reddish-orange acicular crystals; on cooling, orange clusters begin to form; they grow and gradually the whole precipitate becomes orange. After standing for several days in a desiccator over sodium hydroxide, the orange product (the base, the betaine hydrate) loses one molecule of water and is transformed into the betaine.

Found %: H_2O 5.04. $C_{18}H_{18}O_3N_2S \cdot H_2O$. Calculated %: H_2O 5.00.

The betaine forms red or crimson needles melting with decomposition at about 185°. It is insoluble in ether, soluble in acetone, chloroform and nitrobenzene, difficultly soluble in dioxan, very sparingly soluble in hot benzene to form a crimson solution. On standing over a dilute aqueous solution of alkali, the betaine rapidly adds on one molecule of water to form orange crystals of the base (the betaine hydrate).

Found %: N 8.42; S 9.41, 9.40. $C_{18}H_{18}O_3N_2S$. Calculated N 8.18; S 9.36.

3. Tetradecyl bromide of 6-(p-tolylsulfonamido)-quinoline. (6-p-Tolylsulfonamido)-quinoline is heated with a small excess of tetradecyl bromide at 160-170° for 4 hours. The soap-like product is twice crystallized from a small amount of alcohol and ether (yield 20%) and then from alcohol-acetone. White crystals, m.p. 202-204°.

Found %: Br 13.74. $C_{30}H_{43}O_2N_2SBr$. Calculated %: Br 13.83.

4. Tetradecylbetaine of 6-(p-tolylsulfonamido)-quinoline (II). 0.4 g of the tetradecyl bromide of 6-(p-tolylsulfonamido)-quinoline is dissolved in 12 ml 50% alcohol; gradual addition is then made to the hot solution of 2 ml 5% potassium hydroxide, followed by 3 ml water. The precipitate is washed with dilute alcohol and with water and dried in a desiccator over alkali. Two crystallizations from 90% alcohol give yellow crystals (clusters of fine needles) with a waxy softness. The substance does not lose weight when stood over phosphorus pentoxide or when heated in vacuum (30 mm) at 100°. The decomposition temperature of the betaine is about 214°. Trituration of the substance causes the color to change from yellow to red. It is soluble in nitrobenzene and chloroform, insoluble in carbon tetrachloride, almost insoluble in hot benzene; it dissolves to a slight extent in hot dioxan to form a red solution which decolorizes when cooled and separates the yellow betaine. The betaine does not combine with water when stood in a desiccator over a 2 N solution of alkali.

Found %: C 72.40; H 8.74; S 6.72. $C_{30}H_{42}O_2N_2S$. Calculated %: C 72.83; H 8.56; S 6.48.

5. Methyl-p-toluenesulfonate of 6-benzoylaminoquinoline. The starting 6-benzoylaminoquinoline was prepared by reacting 6-aminoquinoline with benzoyl chloride in acetone solution in presence of potassium carbonate, and it was purified by crystallization from dilute alcohol. M.p. 170.5-171° (the literature gives 169° [3]). The compound is converted into the quaternary salt by fusion with the methyl ester of p-toluenesulfonic acid at 180°.

Methyl-p-toluenesulfonate of 6-benzoylaminoquinoline forms slender white needles (from alcohol or water) with m.p. 263-265° (with decomposition), insoluble in benzene. Addition of 25% ammonia to the aqueous solution of the compound leads to a light-yellow coloration; the cooled solution deposits the original salt. Addition of sodium hydroxide to the solution yields a base which comes down as yellow rectangular platelets. When an aqueous solution of the salt made alkaline with sodium hydroxide is shaken with chloroform, the chloroform layer acquires a reddish-brown color.

Found %: S 7.32, 7.40. $C_{24}H_{22}O_4N_2S$. Calculated %: S 7.38.

* The names given to the betaines described in this and previous papers are built upon the principle that each betaine is considered as an alkyl-substituted (with an onium N atom) betainic form of the corresponding amino acid; this nomenclatural principle enables clear recognition of the genetic relation between a betaine and the starting compounds (compare names of compounds 7, 8 and 9). Compounds of this type could also be named, in principal, with reference to the onium function of the molecule, considering the betaine as an inner salt of its corresponding onium base. For example, compound (I) may also be called the betaine of 6-methoxy-8-p-toluenesulfamino-1-methylquinolinium.

6. Methylbetaine of 6-benzoylaminoquinoline [betaine of 6-benzoylamino-1-methylquinolinium] (IIIa). 1 g of methyl-p-toluenesulfonate of 6-benzoylaminoquinoline is dissolved in 60 ml water. To the solution (cooled to 65°) is added dropwise 0.8 ml 10% sodium hydroxide; the solution turns yellow and becomes turbid on further cooling. An additional 9.5 ml 10% sodium hydroxide is gradually added. The resultant crystalline precipitate is filtered after standing for a short period, washed with dilute ammonia solution and then repeatedly with water, and dried in a desiccator over sodium hydroxide. Later the substance is washed with acetone until the filtrate, brown at first, is weakly colored. The yellow crystalline product obtained in a yield of 0.23 g (38%) forms rectangular platelets and is a base (hydrate of the betaine). It is insoluble in dioxan and benzene, soluble in nitrobenzene, pyridine and alcohol. It is unstable in solution. It loses water when stood over P_2O_5 in a vacuum desiccator and is converted into the betaine which forms brown-orange crystals, insoluble in dioxan and benzene. It darkens when heated in a capillary, turns black at about 170°, and gradually begins to melt above 205°.

Found %: N 10.65. $C_{17}H_{14}ON_2$. Calculated %: N 10.68.

When placed in a desiccator over 2 N alkali, the betaine turns yellow and changes into the base. When treated with an alcoholic solution of p-toluenesulfonic acid, the betaine dissolves and then forms a crystalline precipitate which is purified by recrystallization from methyl alcohol. The product is identical with the original methyl-p-toluenesulfonate of 6-benzoylaminoquinoline (m.p. 263-265°; no depression in mixed melting test).

7. 6-(4'-Nitrobenzoylamino)-quinoline. The compound is prepared by acylation of 6-aminoquinoline with p-nitrobenzoyl chloride in presence of sodium bicarbonate [4]. It forms yellow-white crystals after two crystallizations from nitrobenzene. M.p. 256.5-258° (the literature gives 248-250° [4].

8. Methyltoluenesulfonate of 6-(4'-nitrobenzoylamino)-quinoline. Prepared by fusing 6-(4'-nitrobenzoylamino)-quinoline with methyl p-toluenesulfonate at 125-135°. Slender, long, white needles (from dilute alcohol) with m.p. 301.5-303°. Addition of caustic alkali to the aqueous solution of the compound causes deposition of yellow crystals of the base; the base is not precipitated by addition of ammonia or sodium carbonate. When an alkalized solution of the salt is shaken with chloroform, the latter is colored a weak brownish-orange.

Found %: S 6.65, 6.63. $C_{24}H_{21}O_6N_3S$. Calculated %: S 6.69.

9. Methylbetaine of 6-(4' nitrobenzoylamino)-quinoline (IIIb). 1.0 g quaternary salt is dissolved in 60 mg 50% alcohol. To the solution at 70° is slowly added 4 ml 2 N potassium hydroxide; the solution turns orange. On cooling to 40°, a yellow crystalline precipitate begins to come down. A further 2 ml alkali solution is added to the cooled solution. After an hour the precipitate is filtered, washed with dilute alcohol and water and dried in a desiccator over alkali.

The brownish-yellow crystals consist of the base (the betaine hydrate). Yield 0.54 g (79%). The compound is soluble in hot dilute alcohol; it could not be recrystallized, however, due to decomposition when heated. The base loses one molecule of water in vacuum over phosphorus pentoxide and is converted into the betaine.

Found %: H_2O 5.54. $C_{17}H_{13}O_3N_3 \cdot H_2O$. Calculated %: H_2O 5.54.

The betaine forms lustrous red-brown crystals, insoluble in ether and benzene, very sparingly soluble in chloroform. It is slightly soluble in hot pyridine; brief heating causes partial decomposition of the betaine. The crystals blacken when heated in a capillary at a little above 200°; further rise of temperature to 290° does not cause melting. The betaine adds on one molecule of water when stood in a desiccator over dilute caustic alkali.

Found %: N 13.79, 13.93. $C_{17}H_{13}O_3N_3$. Calculated %: N 13.67.

SUMMARY

The preparation and properties of some new bipolar ions of the betaine-azeniate series are described.

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Received May 15, 1951

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THIAZOLIDINE-4-CARBOXYLIC ACID AND ITS DERIVATIVES

III. CONDENSATION OF THIAZOLIDINE-4-CARBOXYLIC ACID AND ITS DERIVATIVES WITH 4-ETHOXYMETHYLENE-2-PHENYL-5(4)-OXAZOLONE

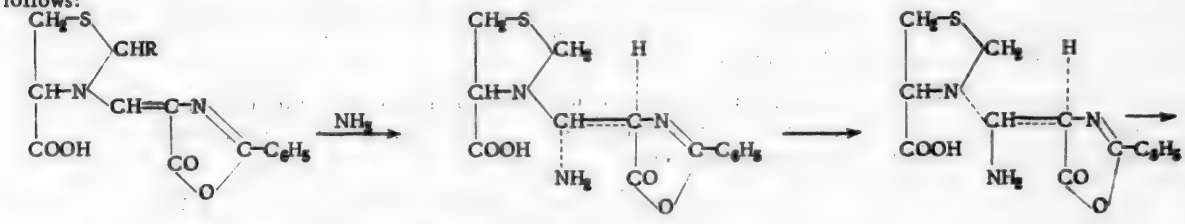
I. T. Strukov

4-Ethoxymethylene-2-phenyl-5(4)-oxazolone is exceptionally reactive. It enters very readily into reaction with ammonia and primary amines to form 4-aminomethylene-2-phenyl-5(4)-oxazolone or the corresponding 4-alkylaminomethylene-2-phenyl-5(4)-oxazolone [1].

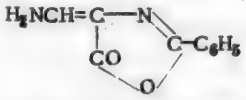
In a study of the chemical properties of 4-aminomethylene-2-phenyl-5(4)-oxazolone it was established that the amino group can be replaced. Thus, on heating this compound with aniline, 4-anilinomethylene-2-phenyl-5(4)-oxazolone was obtained; this had previously been prepared by reacting 4-ethoxymethylene-2-phenyl-5(4)-oxazolone with aniline [1]. Livermore [2] treated dl-benzylpenicilloic acid with sodium hydroxide solution and obtained the crystalline sodium salt of 4-hydroxymethylene-2-benzyl-5(4)-oxazolone. Consequently the amino group in 4-aminomethylene-2-aryl-5(4)-oxazolones is amenable to exchange reactions.

4-Aminomethylene-2-phenyl-5(4)-oxazolone has a good deal in common with acid amides. In fact, 4-hydroxymethylene-2-phenyl-5(4)-oxazolone can be regarded as an acid (the compound titrates with sodium hydroxide); 4-methoxymethylene-2-phenyl-5(4)-oxazolone is reminiscent of the ester of this acid since it is readily saponified by acids and alkalis, while with ammonia it gives 4-aminomethylene derivatives [1]. However, in contrast to acid amides, 4-aminomethylene-2-phenyl-5(4)-oxazolone and its derivatives much more easily exchange their amino group for hydroxyl or another amino group.

It was interesting to determine whether 4-ethoxymethylene-2-phenyl-5(4)-oxazolone is capable of reacting with the imino group of thiazolidine-4-carboxylic acid [3]. Thiazolidine-4-carboxylic acid readily enters into reaction with it in a pyridine medium to form N-(2'-phenyl-5(4)'-oxazolonemethylene-4')-thiazolidine-4-carboxylic acid (I). This compound gives a well-characterized pyridinium salt. On treatment with 4% aqueous ammonia solution, compound (I) is quantitatively decomposed with formation of 4-aminomethylene-2-phenyl-5(4)-oxazolone. It is quite possible that temporary addition of ammonia takes place at the ethylene-imine bond, but this intermediate breaks down and 4-aminomethylene-2-phenyl-5(4)-oxazolone is precipitated. The reaction may be represented as follows:



I R = H
II R = $C_6H_5CH_2$



The reaction proceeds in the same way when 2-benzylthiazolidine-4-carboxylic acid is condensed with 4-ethoxymethylene-2-phenyl-5(4)-oxazolone and there is formed 2-benzyl-N-(2'-phenyl-5(4)'-oxazolonemethylene-4')-thiazolidine-4-carboxylic acid (II). The ammonium salt of this acid is poorly soluble in water so that the reaction proceeds very slowly when the acid is treated with 25% aqueous ammonia solution; however, this reaction also yields 4-aminomethylene-2-phenyl-5(4)-oxazolone.

In their properties, compounds (I) and (II) are reminiscent of N-acylthiazolidine-4-carboxylic acid: they are likewise not susceptible to oxidation by iodine solution, a fact which distinguishes them from thiazolidine-4-carboxylic acid. Indeed, 4-hydroxymethylene-2-phenyl-5(4)-oxazolone possesses strongly marked acidic properties and therefore the aminomethylene group may be compared with an acid amide. The carbon linked to the imino and thio groups in thiazolidine compounds is lacking in the ability to hold these two groups with adequate strength. However, acylation of the imino group suffices to again reduce the strength of the carbon-sulfur bond, and such compounds are already not susceptible to oxidation by iodine. Consequently the acyl group acquires a considerable proportion of the bond energy from the imino group, and it is therefore probable that the bond between nitrogen and carbon is weakened and that between carbon and sulfur is strengthened.

EXPERIMENTAL

N-(2'-Phenyl-5(4)'-oxazolonemethylene-4')-thiazolidine-4-carboxylic acid. 1 g thiazolidine-4-carboxylic acid, 1.6 g 4-ethoxymethylene-2-phenyl-5(4)-oxazolone and 5 ml dry pyridine are stood overnight with periodic stirring. The crystalline precipitate is filtered, washed with ether, and twice recrystallized from acetone; m.p. 158-160° (with decomp.).

The prepared pyridinium salt in 200 ml ether is treated with 10% sulfuric acid. The ethereal solution is washed with water, dried with magnesium sulfate, and the ether distilled off. The residual solid is recrystallized twice from acetone; lustrous yellow crystals with m.p. 209-211° (with decomp.).

6.390 mg substance: 0.525 ml N_2. 6.230 mg substance: 0.516 ml N_2. Found %: N 9.35, 9.47. $C_{14}H_{12}O_4N_2S$. Calculated %: N 9.21.

0.1698 g N-(2'-phenyl-5(4)'-oxazolonemethylene-4')-thiazolidine-4-carboxylic acid is dissolved in 5 ml 4% ammonia solution. After a few minutes white crystals begin to come down. After two hours the mass thickens. The precipitate is filtered, washed with water and dried at 60°. Yield 0.1055 g 4-aminomethylene-2-phenyl-5(4)-oxazolone with m.p. 214-215°. This compound does not depress the melting point of an authentic specimen prepared by the action of alcoholic ammonia on 4-ethoxymethylene-2-phenyl-5(4)-oxazolone.

N-(2'-Phenyl-5(4)'-oxazolonemethylene-4')-2-benzylthiazolidine-4-carboxylic acid. 1 g 2-benzylthiazolidine-4-carboxylic acid, 1 g 4-ethoxymethylene-2-phenyl-5(4)-oxazolone and 5 ml dry pyridine are stood for 24 hours. The precipitate dissolves completely. The reaction mass is diluted with 300 ml ether; the ethereal solution is washed with 2 N phosphoric acid, then with water, and dried with magnesium sulfate. The ether is distilled off to leave a volume of 10-15 ml and the crystals are filtered and washed with ether before recrystallization from acetone. Yield 1.1 g of light-yellow needles with m.p. 190° (with decomp.).

6.690 mg substance: 0.430 ml N_2. Found %: N 7.09. $C_{21}H_{18}O_4N_2S$. Calculated %: N 7.10.

The pyridinium salt was prepared by dissolving acid (II) in a small amount of pyridine. It was recrystallized from a little acetone. Yellow crystals, m.p. 148-150° (with decomp.).

6.015 mg substance: 0.490 ml N_2. 7.515 mg substance: 0.600 ml N_2. Found %: N 8.88, 8.70. $C_{19}H_{18}O_4N_2S$. Calculated %: N 8.87.

Ammonium salt of (II). 0.5 g (II) is dissolved in 30 ml methyl alcohol and a small quantity of strong aqueous ammonia is added until the reaction is weakly alkaline. Microscopic platelets rapidly come down; m.p. 200-204° (with decomp.). Poorly soluble in water.

0.5 g of (II) was treated with 10 ml 25% ammonia solution. The precipitate did not dissolve in the ammonia but gradually acquired a pistachio color. After 10 days the precipitate was filtered and recrystallized from methyl alcohol; m.p. 215-216° (with decomp.). It did not depress the melting point of 4-aminomethylene-2-phenyl-5(4)-oxazolone.

0.1 g of (II) was dissolved in 10 ml ethyl alcohol. The compound was not oxidized when 0.1 g of iodine solution was added.

SUMMARY

Condensation products were prepared from thiazolidine-4-carboxylic acid and its derivatives with 4-ethoxymethylene-2-phenyl-5(4)-oxazolone and consisted of N-(2'-phenyl-5(4)'-oxazolonemethylene-4')-thiazolidine-4-carboxylic acid or its 2-substituted derivatives.

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Received March 12, 1951

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THE SULFONATION REACTION

XXIV. HYDROLYSIS OF NAPHTHALENE DISULFONIC ACIDS

A. A. Spryskov and B. I. Karavaev

The sulfonation of naphthalene at low temperatures is known to yield a mixture of 1,5-, 1,6- and 1,7-naphthalene disulfonic acids [1], whereas at a temperature of 160-180° 2,6-, 2,7-, 1,7- and 1,6-disulfonic acids are formed [2]. Moreover, at 130° the 1,3-disulfonic acid is formed in addition to other sulfonic acids [3]. The quantitative composition of the mixtures has not previously been accurately determined, due mainly to the lack of reliable methods of determination of the individual isomers in a mixture, and also to the constant change in the ratios between the isomers in various reaction conditions.

We believe that the main cause of the change of composition of the sulfonic acid mixtures resides in the different stabilities to desulfurization of the isomers entering into the composition of the sulfonic acid mixtures. If we knew the relative stabilities of the isomers, we could proceed to a systematic investigation of the composition of the sulfonic acid mixtures. This investigation was undertaken with that objective.

It is known that the compounds most stable to hydrolysis are 2,6- and 2,7-naphthalene disulfonic acids; here both the sulfo groups are in the β-position, whereas other isomers containing one or both sulfo groups in the α-position are less stable. It appears from the results of two researches by American authors [4,5] that at 120° and 140° the 1,5-disulfonic acid is less readily hydrolyzed than the 1,6-acid, but this appears improbable because the 1,5-isomer has both sulfo groups in the α-position.

In these researches the hydrolysis was performed in presence of sulfuric acid of definite concentrations, but the invariable presence of the hydrolyzing agent (water) was ignored. This is one of the sources of error. Moreover, the American authors arrived at the erroneous conclusion that the reaction does not proceed stepwise and that the sulfo groups are split off simultaneously [6] without intermediate formation of monosulfonic acids.

In a study of the desulfurization of four naphthalene disulfonic acids, Lantz [7] found that that 2,6- and 2,7-disulfonic acids are desulfurized with the same velocity. The 1,5- and 1,6-isomers are also desulfurized with identical velocities but much more readily than the 2,6- and 2,7-isomers

We have investigated the relative resistance to hydrolysis of all the six naphthalene disulfonic acids formed by direct sulfonation. We endeavored to perform a series of experiments in conditions close to those in which the formation and rearrangement of the isomers occurs, i.e. in presence of sulfuric acid. However, the concentration of the latter must not reach such values that the naphthalene formed on hydrolysis is resulfonated. In order to find the concentration of sulfuric acid permissible for hydrolysis, a series of experiments on the sulfonation of naphthalene and of naphthalene β-sulfonic acid was carried out. Results are presented in Tables 1 and 2.

The first two experiments of Table 1 showed that 60-66% sulfuric acid does not sulfonate naphthalene to a substantial extent at 160° because the naphthalene does not dissolve in acid of this concentration [8].

In presence of a sulfonic acid, however, naphthalene is soluble in the mixture. Experiments 157 and 158, carried out in presence of m-benzene disulfonic acid, which is not sulfonated or hydrolyzed in these conditions, showed that naphthalene is sulfonated by 50% sulfuric acid with considerable speed. In the experiments on hydrolysis at 160°, therefore, sulfuric acid was not used in concentrations higher than 45% in order to exclude or reduce to a minimum the possibility of resulfonation of the naphthalene. Table 2 contains data for the sulfonation of naphthalene β-sulfonic acid at a temperature of 100°; these data show that only 66% sulfuric acid is substantially without sulfonating action on the β-acid.

Experiments on the hydrolysis of naphthalene disulfonic acids at a temperature of 161° are detailed in Table 3. The first series of experiments was performed in the absence of sulfuric acid, the second and third series in presence of 35 and 45% sulfuric acid, and in each case in presence of about 9 mole water per mole

of disulfonic acid. The experiments show that the disulfonic acids can be arranged in the following order in respect of resistance to hydrolysis:

2,6- > 2,7- > 1,3- > 1,7- > 1,6- > 1,5-

In this series the 2,6- and 2,7- isomers differ markedly from the other isomers. They are many times more stable than the disulfonic acids with the sulfo group in the α-position. The 1,5-disulfonic acid also differs considerably from the α- and β-acids. It is substantially completely decomposed in the described conditions and is therefore not present in the sulfonic acid mixtures prepared at 160°.

TABLE 1

Sulfonation of Naphthalene at 161° ± 1°

Expt. No.	Taken				Duration (hours)	% Conc. of sulfuric acid in mixture	Amount of sulfuric acid reacted (%)
	m-Benzene disulfonic acid (g)	Naphthalene (g)	Sulfuric acid (g)	Water per mole disulfonic acid (moles)			
140a	–	1.01	3.214	–	18	60.2	0.4
140b	–	1.38	4.442	–	4	66.1	0.0
157	0.3189	0.5	–	8.76	20	58.9	26.8
158	0.3257	0.5	–	9.71	20	49.9	14.2

TABLE 2

Sulfonation of Naphthalene-Sulfonic Acid at 100° for 25 hours•

Expt. No.	Moles water in mixture per mole sulfonic acid	% Conc. of sulfuric acid	Amount of β-acid sulfonated (in %)	Conc. of H_2SO_4 in mixture after expt (%)
194	4.75	78.1	37.8	74.4
195	4.55	74.8	16.5	72.8
196	4.51	70.2	2.7	69.8
197	4.42	66.1	0.4	65.8

In Table 4 are presented the results of experiments at 124°. At this temperature the 2,6- and 2,7-isomers are hydrolyzed extremely slowly, so that no experiments were performed with them. The isomers containing the sulfo group in the α- and β-position are hydrolyzed almost exclusively to the monosulfonic acid, i.e. they only split off the sulfo group in the α-position, whereas the 1,5-acid in presence of sulfuric acid is hydrolyzed preferentially to naphthalene.

At a temperature of 100° the hydrolysis of the disulfonic acids proceeds very slowly (Table 5). On changing from 45% sulfuric acid to 65%, the speed of hydrolysis is roughly doubled.

Whereas at a temperature of 125° only α-β-disulfonic acids are hydrolyzed to monosulfonic acid, at 100° all the sulfonic acids containing a sulfo group in the α-position lose only one sulfo group in the described conditions. The order of stability of the isomers to hydrolysis remains the same in all cases as above.

Finally, experiments were performed on heating of the 1,5-disulfonic acid with 60 % sulfuric acid at a temperature of 64° for periods of 40 and 120 hours. Analysis of the mixture showed, however, that the acid is not appreciably hydrolyzed in these conditions.

Consequently, the statement of Ambler and Scanlan [6] concerning the simultaneous removal of both sulfo groups is in conflict with our experimental results. The American authors were unable to detect any traces of the β-sulfonic acid during hydrolysis of the 1,6-disulfonic acid [6]. We performed an experiment on the hydrolysis of the 1,6-acid by heating in 35% sulfuric acid at 160° for 5 hours. After determination of the naphthalene in the mixture, a part of the solution was analyzed as described below, and another portion was analyzed for the β-sulfonic acid content by the method of Chuksanova and Bilik [9], involving salting-out with common salt and reprecipitation in the form of the benzidine salt. It was found that 5.3% of disulfonic acid was hydrolyzed to naphthalene and 50.7% to monosulfonic acid. The amount of β-sulfonic acid in the form of the benzidine salt was also found to be 50.7%.

• To an accurately weighed sample of 0.4-0.6 g of β-acid, was added the calculated amount of sulfuric acid.

TABLE 3

Hydrolysis of Naphthalene Disulfonic Acids at a Temperature of 161° ± 1°

Expt. No.	Isomer	Duration of heating (hours)	Moles water per mole disulfonic acid	Conc. of sulfuric acid in mixture		% of original disulfonic acid hydrolyzed	
				initial	final	to naphthalene	to monosulfonic acid
230	2,6-	25	9.14	0		traces	2.0
229	2,7-	25	9.10	0		traces	3.5
162	1,3-	25	8.86	0	36.0	21.9	39.4
161	1,7-	25	8.89	0	40.7	20.1	59.1
160	1,6-	25	8.97	0	44.1	26.0	61.4
159	1,5-	25	9.04	0	58.9	97.1	–
184	2,6-	75	9.00	34.1	40.2	5.3	12.1
185	2,7-	75	9.10	34.9	45.1	9.9	21.4
170	1,3-	5	9.04	34.2	41.8	2.7	23.7
174	1,7-	5	9.18	35.0	51.5	traces	62.0
168	1,6-	5	8.99	34.4	51.8	5.9	64.1
173	1,5-	5	8.84	35.0	64.9	61.0	37.0
191	2,6-	25	8.94	45.8	47.9	2.5	5.9
190	2,7-	25	8.95	45.2	48.3	3.6	8.0

TABLE 4

Hydrolysis of Naphthalene Disulfonic Acids at 191° ± 1° for 25 hours

Expt. No.	Isomer	Moles water per mole disulfonic acid	Conc. of sulfuric acid in mixture		% of disulfonic acid hydrolyzed	
			initial	final	to naphthalene	to monosulfonic acid
178	1,3-	8.93	–	–	traces	1.1
177	1,7-	9.01	–	–	traces	1.9
176	1,6-	9.04	–	–	0	5.3
175	1,5-	9.14	–	–	3.0	3.5
182	1,3-	9.04	34.6	36.6	traces	7.3
181	1,7-	8.94	33.8	37.0	traces	10.8
180	1,6-	9.24	35.9	39.7	0.4	14.1
179	1,5-	9.45	34.4	46.1	21.6	6.6

TABLE 5

Hydrolysis of Naphthalene Disulfonic Acids at 100° ± 0.5° for 100 hours

Expt. No.	Isomer	Moles water per mole disulfonic acid	Conc. of sulfuric acid in mixture		% of disulfonic acid hydrolyzed	
			initial	final	to naphthalene	to monosulfonic acid
189	1,3-	9.08	45.0	–	none	2.8
188	1,7-	8.95	44.9	–	none	3.6
187	1,6-	9.23	45.4	–	traces	3.6
186	1,5-	9.13	45.3	–	traces	5.4
201	1,3-	8.93	65.8	66.3	none	5.5
200	1,7-	8.97	65.2	65.8	none	7.0
199	1,6-	9.09	64.8	65.4	none	7.2
198	1,5-	9.22	65.1	65.8	traces	8.0

EXPERIMENTAL

All the hydrolysis experiments were performed in sealed tubes which were heated in batches of 2, 4 or 6 in an Eyckman apparatus with the vapors of butyric acid, ethyl butyrate and water. Starting materials were the free disulfonic acids prepared by hydrolysis in an aqueous alcoholic medium of the corresponding disulfochlorides. They were identified by their melting points. After hydrolysis, the contents of the tubes were poured into water and the naphthalene filtered through a small porcelain crucible with a perforated bottom. The precipitate was dried over lumps of sodium hydroxide in a desiccator saturated with naphthalene vapor. Blank experiments showed that the loss is about 0.003 g for a sample of naphthalene weighing about 0.2 g. This correction was introduced into the determination.

Following the removal of the naphthalene, the sulfuric acid in the filtrate was determined gravimetrically as barium sulfate. The increase in the amount of sulfuric acid after hydrolysis and the weight of separated naphthalene enabled calculation of the amount of disulfonic hydrolyzed to naphthalene and to monosulfonic acid.

SUMMARY

1. Six isomeric naphthalene disulfonic acids formed by direct sulfonation of naphthalene were subjected to hydrolysis at temperatures of 161, 124 and 100° in water and in sulfuric acid with concentrations of 35 to 65%.

The disulfonic acids exhibit the following order of stability to hydrolysis: 2,6- > 2,7- > 1,3- > 1,7- > 1,6- > 1,5-.

2. Hydrolysis proceeds stepwise. At first one sulfo group is split off to form a monosulfonic acid, which then hydrolyzes to naphthalene.

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Received March 23, 1951

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SYNTHESIS OF N-OXIDES OF PHENAZINE DERIVATIVES

I. MONO-N-OXIDES OF ALKOXYPHENAZINES

V. P. Chernetsky and A. I. Kiprianov

N-Oxides of phenazine derivatives have been little investigated. Mono-N-oxides of phenazine were prepared for the first time by Wohl [1] in 1901 by alkaline condensation of nitrobenzene with aniline, but Wohl failed to obtain N-oxides by direct oxidation of phenazine. This was accomplished in 1938 by Z. V. Pushkareva and G. I. Agibalova [2] who obtained di-N-oxides of phenazine for the first time by oxidizing phenazine with perbenzoic acid in chloroform. Other investigators [3,4] prepared several mono- and di-N-oxides of phenazine derivatives (mono-N-oxides of 2,6-dihaloderivatives of phenazine, the di-N-oxide of 2-chlorophenazine, etc.).

In 1949 A. I. Kiprianov, S. B. Serebryanyi and V. P. Chernetsky established the structure [5] and effected the synthesis [6] of the natural pigment, iodinin – the di-N-oxide of 1,5-dihydroxyphenazine.

The present paper relates to a series of mono-N-oxides of alkoxyphenazines not previously described in the literature: mono-N-oxides of 1-methoxyphenazine, 1-ethoxyphenazine, 1,5-diethoxyphenazine, 1,6-diethoxyphenazine, 1,7-dimethoxyphenazine, 1,8-diethoxyphenazine and 2,6-dimethoxyphenazine (see table).

All the mono-N-oxides, with exception of (VII), were prepared by direct oxidation of the corresponding bases with hydrogen peroxide in acetic acid or with perbenzoic acid in benzene. The synthesis of the bases has been already described in publications from our laboratory [7,8,9]; some of them were kindly placed at our disposal by S. B. Serebryanyi to whom we take this opportunity of expressing our thanks.

2,6-Dimethoxyphenazine mono-N-oxide (VII) was prepared directly by alkaline condensation of p-nitroanisole with p-anisidine. It should be noted that mono-N-oxides are nearly always formed in the alkaline condensation of aromatic amines with aromatic nitro compounds, with the aim of preparing phenazine derivatives.

Direct oxidation of bases with perbenzoic acid, in the case of some phenazine derivatives, gives both mono-N-oxides and di-N-oxides.

Fractionation and purification of the prepared N-oxides was effected by chromatography on alumina followed by crystallization. When washing out the column with solvent, the compounds were always washed out in a definite sequence. The unoxidized base was the first to be washed out from the bottom pale-yellow band; then the mono-N-oxide was extracted from the following bright-yellow band. In some cases there was a red band of di-N-oxide higher up.

The mono-N-oxides have fairly high solubility in organic solvents. The yellow solutions exhibit an intense green fluorescence. They are sparingly soluble in water. Dialkoxyphenazine mono-N-oxides are less soluble than monoalkoxyphenazine mono-N-oxides. The mono-N-oxides dissolve in dilute acids with a red color.

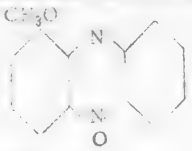
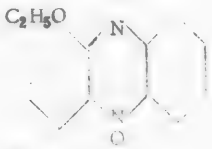
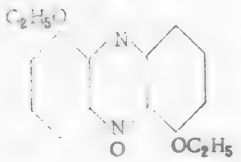
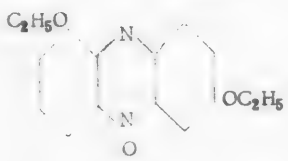
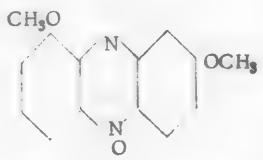
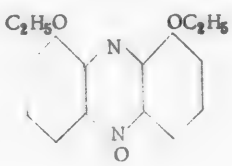
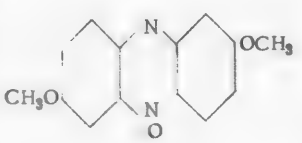
All the N-oxides are decomposed when heated. The mono-N-oxides of monoalkoxyphenazines have a melting point 10-15° lower than the decomposition temperature.

EXPERIMENTAL

1-Methoxy- and 1-ethoxyphenazines were oxidized in the following manner.

A weighed amount of the base was dissolved in glacial acetic acid in a vessel equipped with stirrer, reflux condenser and dropping funnel. The solution was heated on a water bath to 50-55° and addition made in several portions in the course of 10-12 hours of 10-20 times the amount (calculated on the base) of a 30% solution of hydrogen peroxide. The solution gradually darkened. After 15 hours the dark liquid was run off into 5 times the amount of water. The precipitate was filtered, and washed with dilute acetic acid and water. The dried oxidation product was dissolved in chloroform, filtered from undissolved impurities and the chloroform evaporated. Depending upon the purity, the product either crystallized or was subjected to supplementary chromatographic treatment on alumina.

Mono-N-oxides of Alkoxy Derivatives of Phenazine

Prep.	Name of base	Formula of mono-N-oxide	Melting and decomposition point	Appearance
I	1-Methoxyphenazine		196-198° (m.p.) 210° (decomp.)	Greenish-yellow platelets
II	1-Ethoxyphenazine		181-182° (m.p.) 214-217° (decomp)	Yellow needles
III	1,5-Diethoxyphenazine		170-172° (decomp)	Orange-yellow needles
IV	1,6-Diethoxyphenazine		207-209° (decomp)	Bright-yellow needles
V	1,7-Dimethoxyphenazine		227-229° (decomp)	Golden yellow needles
VI	1,8-Diethoxyphenazine		218-222° (decomp)	Yellow platelets
VII	2,6-Dimethoxyphenazine		233-235° (decomp)	Yellow silky needles

1-Methoxyphenazine mono-N-oxide (I). 0.5 g 1-methoxyphenazine was oxidized using 10 ml glacial acetic acid and 10 ml 30% hydrogen peroxide. After evaporation of the chloroform there remained reddish-yellow leaflets. Weight 0.3 g (58.5% of theory), m.p. 185-190°, decomp. pt. 208-210°. Recrystallization from hot water gave golden yellow platelets (the color changed to dull orange on drying), m.p. 196-198°, decomp.pt. 210° *.

* All temperature values are corrected. The melting point of the preparations was determined twice: once with rapid heating the melting point was observed approximately; the second time the apparatus was heated to a temperature 5-10° lower; the thermometer and capillary were then inserted and the temperature raised at the rate of 1° per minute until the substance decomposed.

Found %: N 12.20, 12.37*. $C_{13}H_{10}O_2N_2$. Calculated %: N 12.39.

1-Ethoxyphenazine mono-N-oxide (II). 0.5 g 1-ethoxyphenazine was oxidized in 10 ml glacial acetic acid with 10 ml 30% hydrogen peroxide. The residue after removal of the chloroform consisted of red-brown crystals. Weight 0.38 g. The melting point was gradual (90-160°). It was dissolved in benzene and chromatographed on alumina. After distilling off the benzene in vacuum, the residue was dried in the air. Weight 0.25 g (46.5% of theory), m.p. 176-180° decomp. pt. 214-217°. Clusters of slender yellow needles were formed from hot water with addition of alcohol: m.p. 181-182°, decomp. pt. 214-217°.

Found %: N 11.54, 11.63. $C_{13}H_{12}O_2N_2$. Calculated %: N 11.66.

Preparation of mono-N-oxides of (III), (IV), (V), (VI). 1,5-, 1,6-, 1,8-diethoxyphenazines and 1,7-dimethoxyphenazine were oxidized with perbenzoic acid in dry benzene. Weighed amounts of the bases were dissolved in benzene, the amount of the latter varying with the solubility of the substances. To the benzene solutions of the bases was added a benzene solution of perbenzoic acid containing 4 g-equivalents of acid. The mixture was stood at room temperature for 5 days. The yellow solutions gradually turned red-orange and small precipitates came down. At the end of 5 days the benzene solutions of the oxidation products were filtered and chromatographed in columns with alumina. On washing the columns with solvent (benzene, chloroform, dichlorethane) in all cases the chromatogram contained at the bottom a pale-yellow band of base, above this a bright-yellow band of mono-N-oxide and, in some cases, still higher up a small red band of di-N-oxide. Solutions of the substances washed out of the columns were collected separately. The solvent was distilled off in vacuum and the residue evaporated in the air. The products were crystallized from chloroform or aqueous alcohol. Chromatography and crystallization were repeated in some cases to obtain pure substances.

1,5-Diethoxyphenazine mono-N-oxide (III). 0.2 g 1,5-diethoxyphenazine in 100 ml benzene was oxidized with 0.5 g perbenzoic acid in 10 ml benzene. After two chromatographic treatments there was obtained 85 mg (40% of theory) of yellow-orange needles. M.p. 170-172° (with decomp). Found %: N 9.82 , 9.64. $C_{16}H_{16}O_3N_2$. Calculated %: N 9.85.

1,6-Diethoxyphenazine mono-N-oxide (IV) 0.2 g 1,6-diethoxyphenazine in 50 ml benzene was oxidized with 0.5 g perbenzoic acid in 10 ml benzene. Yield 145 mg (68.5% of theory) of yellow crystals. M.p. 185° (with decomp). The substance was twice recrystallized, once from aqueous acid and then from aqueous alcohol, forming clusters of bright-yellow needles. M.p. 207-209° (with decomp). Found %: N 10.02, 10.06. $C_{16}H_{16}O_3N_2$. Calculated %: N 9.85.

1,7-Dimethoxyphenazine mono-N-oxide (V). 0.2 g 1,7-dimethoxyphenazine in 50 ml benzene was oxidized with 0.5 g perbenzoic acid in 10 ml benzene to give 76 mg (35.5% of theory) of a yellow compound. M.p. 205-210° decomp. pt. 220°. Two crystallizations from aqueous alcohol gave clusters of golden yellow needles. M.p. 227-229° (with decomp). Found %: N 11.09, 11.12. $C_{14}H_{12}O_3N_2$. Calculated %: N 10.98.

1,8-Diethoxyphenazine mono-N-oxide (VI). 0.2 g 1,8-diethoxyphenazine in 100 ml benzene was oxidized with 0.5 g perbenzoic acid in 10 ml benzene to give 160 mg (75.5% of theory) of a brown crystalline substance. M.p. 208-210° (with decomp). From aqueous alcohol: golden yellow platelets with m.p. 218-222° (with decomp). Found %: N 9.79, 9.94. $C_{16}H_{16}O_3N_2$. Calculated %: N 9.85.

2,6-Dimethoxyphenazine mono-N-oxide (VII). 10 g p-nitroanisole was mixed with 10 g p-anisidine and the mixture was fused. To the fused mixture with energetic shaking was added in small portions 40 g potassium hydroxide powder. The mixture heated up considerably during addition of the alkali and darkened. The reaction vessel was cooled by running water in order to prevent the temperature from rising above 100°. After addition of the whole of the alkali and cooling of the reaction mass to room temperature, the mass was kept for 10 days. At the end of this period the mass was steam-distilled. The residue in the flask was cooled and the solid product filtered from the aqueous alkaline mother liquor. The solid, nearly black, product was dried and chromatographed from chloroform solution in a column with alumina. 1.75 g (10.5%) of mono-N-oxide fraction was obtained as orange-yellow crystals with m.p. 230-232° (with decomp). Crystallization from chloroform gave yellow silky needles melting at 233-235° (with decomp).

Found %: N 10.96, 10.72. $C_{14}H_{12}O_3N_2$. Calculated %: N 10.98.

* Nitrogen was determined by microanalysis.

SUMMARY

1. The corresponding mono-N-oxides were prepared by oxidation of 1-ethoxyphenazine with hydrogen peroxide in acetic acid and of 1,5-, 1,6-, 1,8-diethoxyphenazines and of 1,7-dimethoxyphenazine with perbenzoic acid in benzene.

2. Alkaline condensation of p-nitroanisole with p-anisidine gave the mono-N-oxide of 2,6-diemthoxyphenazine.

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Received May 15, 1951

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* See Consultants Bureau translation, p. 1691.
** See Consultants Bureau translation, p. 2265.

SYNTHESIS OF SOME ANALOGS OF PHENYLALANINE

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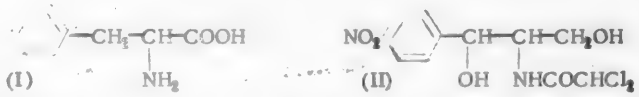
A comparison of the formulas of one of the most important metabolites of the animal organism, phenylalanine (I), and chloromycetin (II) shows that these substances have very similar structures.



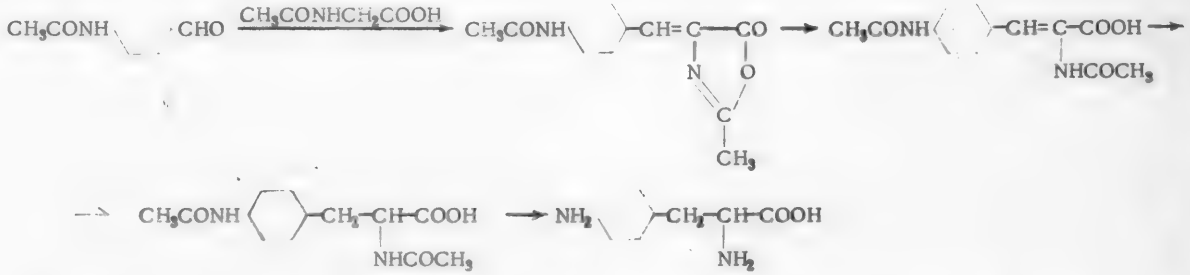
In this connection we planned to introduce into the phenylalanine molecule some functional groups characteristic of chloromycetin. In particular it was of interest to synthesize a phenylalanine containing a nitro group in the para-position of the aromatic nucleus and a dichloroacetyl residue at the α-amino group.

Phenylalanine, the starting substance for this synthesis, was prepared by the known method from α-acetaminocinnamic acid [1]. Reduction of α-acetaminocinnamic acid was effected by catalytic hydrogenation in presence of skeletal nickel catalyst in an autoclave at 70-90° and a hydrogen pressure of 25-30 atm. Nitration of phenylalanine was performed with fuming nitric acid in presence of concentrated sulfuric acid [2] at 0°. p-Nitro-N-dichloroacetylphenylalanine was prepared by the action of an ethereal solution of dichloracetyl chloride on an aqueous alcoholic solution of p-nitrophenylalanine.

At the end of 1950, after our investigation had been completed, a paper was published by Woolley [3] in which the author details the synthesis of some analogs of phenylalanine and, in particular, of p-nitro-N-dichloroacetylphenylalanine. He prepared this substance by nitration of N-dichloroacetylphenylalanine. It had m.p. 177-179°. In support of the structure, the author only gave the nitrogen determination without weights. The wide discrepancy between the melting points of our substance (169-170°) and that synthesized by Woolley remains mysterious, all the more since reduction of the p-nitro-N-dichloroacetylphenylalanine prepared by us led to the formation of p-amino-N-dichloroacetylphenylalanine.

In connection with the fact that the presence of an amino group in the aromatic nucleus has great significance for the antitubercular action of preparations, it appeared expedient to introduce this group into the phenylalanine molecule together with the dichloroacetyl residue.

p-Aminophenylalanine has up to now been prepared only by reduction of p-nitrophenylalanine [2]. We have developed a more convenient method of preparation from p-acetaminobenzaldehyde. The synthesis is represented by the following scheme:



p-Acetaminobenzaldehyde, prepared by the method evolved in our laboratory [4], reacts with acetylglycine to form the azlactone of α,p-diacetaminocinnamic acid, saponification of which yields the acid. α,p-Diacetaminocinnamic acid was hydrogenated with hydrogen in presence of skeletal nickel catalyst at 80-100° and 30 atm in sodium bicarbonate solution forming p-acetamino-N-acetylphenylalanine; this is converted by acid hydrolysis into p-aminophenylalanine. Treatment of p-aminophenylalanine with dichloracetyl chloride gave p-dichloroacetamino-N-dichloroacetylphenylalanine.

In addition to the compounds mentioned above, the methyl esters of p-nitro-N-dichloroacetylphenylalanine and p-dichloroacetamino-N-dichloroacetylphenylalanine were prepared.

EXPERIMENTAL

p-Nitro-N-dichloroacetylphenylalanine. To a solution of 1.4 g p-nitrophenylalanine in 25 ml 1 N sodium hydroxide solution is gradually added, with ice-water cooling and stirring, 1.5 g dichloroacetyl chloride in 10 ml ether. After the addition, the flask contained a fairly large precipitate. The mixture is stirred for another 20 minutes, after which the ether is removed in vacuum. The precipitate dissolves during this operation. The solution is acidified with 10% hydrochloric acid until acid to congo and the precipitate is filtered off, washed with glacial acetic acid and dried. Yield 1.6 g, m.p. 164-169°. After recrystallization from aqueous alcohol, p-nitrodichloroacetylphenylalanine forms colorless crystals with m.p. 169-170°.

2.999 mg substance: 4.525 mg CO_2; 0.960 mg H_2O. 5.520 mg substance: 0.431 ml N_2 (23°, 733.0 mm). 3.040 mg substance: 2.735 mg AgCl. Found %: C 41.15; H 3.58; N 8.68; Cl 22.26. $C_{11}H_{10}O_5N_2Cl_2$. Calculated %: C 41.12; H 3.11; N 8.72; Cl 22.11.

Methyl ester of p-nitrophenylalanine hydrochloride. 2.62 g p-nitrophenylalanine and 25 ml 4.5% hydrogen chloride solution in methanol are heated at the boil on the water bath for 3 hours. The excess of hydrogen chloride and methanol is then driven off in vacuum to leave 3 g white crystals which were twice recrystallized from alcohol. M.p. 197°.

5.562 mg substance: 4.35 ml 0.01 N H_2SO_4 (Kjeldahl). Found %: N 10.94. $C_{10}H_{13}O_4N_2Cl$. Calculated %: N 10.74.

Methyl ester of p-nitro-N-dichloroacetylphenylalanine. To a solution of 3 g methyl ester of p-nitrophenylalanine hydrochloride in a little water is added dropwise an excess of 25% aqueous ammonia. The resultant oil is extracted with ether, the ethereal solution dried with sodium sulfate and the ether driven off in vacuum to leave 2.2 g of yellow oily material – the methyl ester of p-nitro-N-dichloroacetylphenylalanine. To this substance, dissolved in 15 ml ether is added gradually with cooling and stirring, alternately, a 2.5% solution of sodium hydroxide and a solution of 2 g dichloroacetyl chloride in 10 ml ether at such a rate that the reaction is weakly alkaline the whole time. At the conclusion of the reaction a white crystalline precipitate is formed which is filtered (after removal of ether), washed with 5% hydrochloric acid, then with 5% sodium carbonate and with water, and dried. Yield 2 g with m.p. 127-129°. After recrystallization from aqueous alcohol the methyl ester of p-nitro-N-dichloroacetylphenylalanine has m.p. 129-130°.

4.282 mg substance: 6.745 mg CO_2; 1.380 mg H_2O. Found %: C 42.96; H 3.60. $C_{12}H_{12}O_5N_2Cl_2$. Calculated %: C 42.98; H 3.58.

p-Amino-N-dichloroacetylphenylalanine. A solution of 1 g p-nitro-N-dichloroacetylphenylalanine in 20 ml ethyl alcohol is subjected to catalytic hydrogenation with hydrogen in presence of skeletal nickel catalyst at room temperature and atmospheric pressure. Hydrogen is absorbed slowly (in the course of 6 hours) and during the process a part of the formed substance crystallizes out. To the reaction mixture is added 15 ml alcohol, the mixture is heated to the boil and the catalyst is filtered from the hot solution.

Partial evaporation of the alcoholic solution, followed by cooling, results in separation of 0.5 g of faint-yellow crystals with m.p. 182-183°.

5.580 mg substance: 0.488 ml N_2 (240°, 726 mm). 5.485 mg substance: 0.488 ml N_2 (26.5°, 726 mm). Found %: N 9.60, 9.69. $C_{11}H_{12}O_3N_2Cl_2$. Calculated %: N 9.62.

Azlactone of α-p-diacetaminocinnamic acid. A mixture of 32 g p-acetaminobenzaldehyde, 25 g acetylglycine, 17 g fused sodium acetate and 56 g acetic anhydride is heated under a reflux condenser on the boiling water bath for 4 hours. The precipitate at first dissolves; later yellow crystals of the azlactone are precipitated. The precipitate is quickly filtered hot at the pump, washed several times with small portions of alcohol and dried. Yield 31 g. Several recrystallizations from aqueous alcohol give yellow crystals, insoluble in bicarbonate and water, readily soluble in alcohol, m.p. 230-232°.

3.365 mg substance: 7.845 mg CO_2; 1.529 mg H_2O. Found %: C 63.58; H 5.08. $C_{13}H_{12}O_3N_2$. Calculated %: C 63.90; H 4.95.

α,p-Diacetaminocinnamic acid. 1.33 g recrystallized azlactone of α,p-diacetaminocinnamic acid, 20 ml acetone and 7 ml water are boiled on the water bath for 8 hours. After the heating the whole of the azlactone goes into solution. The acetone and water are removed in vacuum and the residue dissolved in alcohol; the solution is

decolorized with carbon, filtered and cooled with ice mixture. The separated crystals are filtered, washed with small amounts of alcohol and ether. Yield 1.05 g of α,p-diacetaminocinnamic acid with m.p. 240-241°. The acid crystallizes from aqueous alcohol with one molecule of water; from 96% alcohol it comes out without water of crystallization.

4.322 mg substance: 9.459 mg CO_2; 2.102 mg H_2O. 6.490 mg substance: 0.621 ml N_2 (22.0°, 726.0 mm). Found %: C 59.68; H 5.44; N 10.57. $C_{13}H_{14}O_4N_2$. Calculated %: C 59.54; H 5.34; N 10.68.

p-Acetamino-N-acetylphenylalanine. 12.75 g unrecrystallized α,p-diacetaminocinnamic acid is dissolved in 150 ml 3% sodium bicarbonate solution. The slightly turbid yellow solution of the salt is decolorized with active carbon and subjected to catalytic hydrogenation in presence of skeletal nickel catalyst at 80-100° and 30 atm for 3 hours. After removal of the catalyst, the filtrate is evaporated in vacuum to a volume of about 40 ml, acidified with 10% hydrochloric acid until acid to congo, cooled with ice and filtered. The p-acetamino-N-acetylphenylalanine is washed with ice water. After drying in a vacuum desiccator, the acid had m.p. 208-210°; yield 11.35 g. After recrystallization from hot water the m.p. was 210-211°.

3.702 mg substance: 8.008 mg CO_2; 2.068 mg H_2O. Found %: C 59.00; H 6.25. $C_{13}H_{16}O_4N_2$. Calculated %: C 59.09; H 6.06.

p-Aminophenylalanine. A mixture of 1 g p-acetamino-N-acetylphenylalanine and 32 ml 1 N hydrochloric acid is heated to boiling for 20 hours. The solution is then evaporated in vacuum and the residual thick, caramelized syrup is treated with water several times and the latter then distilled off in vacuum. The hydrochloride is then dissolved in a small quantity of water and neutralized with ammonia. Acetic acid is added until the reaction is acid, when white crystals come down which are filtered, washed with a small quantity of ice water and dried.

After recrystallization from aqueous alcohol and drying in a vacuum desiccator at 100°, the substance has m.p. 221-222° (with decomp). According to the literature, p-aminophenylalanine melts at 245° (with decomp).

3.918 mg substance: 8.631 mg CO_2; 2.412 mg H_2O. Found %: C 59.60; H 6.89. $C_9H_{12}O_2N_2$. Calculated %: C 60.00; H 6.66.

p-Dichloroacetamino-N-dichloroacetylphenylalanine. To a solution of 2.5 g p-aminophenylalanine in 25 ml 2.5% NaOH with cooling and stirring are alternately added a solution of 5.5 g dichloroacetyl chloride in 10 ml ether and a 2.5% aqueous solution of NaOH at such a rate that the reaction is alkaline over the whole period. During the reaction an oil is formed, which at the end crystallizes. The ether is removed in vacuum, the residue acidified with hydrochloric acid until it gives an acid reaction to congo, and the white precipitate is filtered, washed with ice water and dried in a vacuum desiccator. Yield 2.35 g.

After two recrystallizations, p-dichloroacetamino-N-dichloroacetylphenylalanine has m.p. 215-216°. White crystals, insoluble in hydrochloric acid and water, readily soluble in alcohol.

3.292 mg substance: 4.682 mg CO_2; 0.896 mg H_2O. 5.146 mg substance: 2.64 ml 0.01 N H_2SO_4. (Kjeldahl). Found %: C 38.79; H 3.04; N 7.18. $C_{13}H_{12}O_4N_2Cl_4$. Calculated %: C 38.80; H 2.98; N 6.96.

Methyl ester of p-dichloroacetamino-N-dichloroacetylphenylalanine. 4.3 g of the hydrochloride of p-aminophenylalanine and 25 ml 4.5% solution of hydrogen chloride in methanol are boiled on the water bath for 6 hours. The solution is then evaporated in vacuum and the residue (a thick, caramelized syrup) is dissolved in 30 ml water and neutralized with aqueous ammonia. The ester of p-aminophenylalanine does not separate at this stage. The solution is evaporated to dryness and the resultant thick resin, contaminated with ammonium chloride crystals, is dissolved in 15 ml water. With cooling and stirring, alternate addition is made to this solution of 6.5 g dichloroacetyl chloride in 20 ml ether and a 2.5% aqueous solution NaOH, at such a speed that the reaction is always weakly alkaline. At the conclusion of the reaction an oil separates and immediately crystallizes. The reaction mixture is acidified with hydrochloric acid until acid to congo and the precipitate is filtered, washed with water and dried. After recrystallization from a little alcohol the substance melts at 175-176°.

4.111 mg substance: 6.121 mg CO_2; 1.279 mg H_2O. Found %: C 40.61; H 3.48. $C_{14}H_{14}O_4N_2Cl_4$. Calculated %: C 40.38; H 3.36.

SUMMARY

1. A series of new derivatives of phenylalanine containing the dichloroacetyl group has been prepared.

2. A new method for preparation of p-aminophenylalanine from p-acetaminobenzaldehyde has been developed.

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[1] Organic Syntheses, Collective Vol. II, pp. 69, 72, 498.

[2] Erlenmeyer, Lipp, Ann., 219, 213 (1883).

[3] Woolley, J. Biol. Chem., 185, N 1, 293 (1950).

[4] M. N. Shchukina and E. D. Sazonova, Author's Cert. No. 11270 (1950).

Received March 12, 1951

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INVESTIGATIONS ON AMINO ACIDS

III. CIS-TRANS ISOMERISM IN THE OXAZOLONE (AZLACTONE) SERIES

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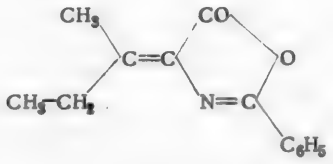
Workers [1] who investigated the condensation of ketones with hippuric acid arrived at the conclusion that certain ketones, including methylethyl ketone, do not react with the acid. Instead of the anticipated oxazolones, they obtained a compound with m.p. 138° and the empirical formula $(C_9H_7O_2N)_x$, apparently a product of condensation of hippuric acid molecules. However, when we condensed methylethyl ketone with hippuric acid we obtained, in place of the compound with m.p. 138°, a reddish-yellow oil which changed on standing into crystals with m.p. 33-37°. The empirical formula of this compound is $C_{13}H_{13}O_2N$. On the assumption that this is the sought for oxazolone (A), we decided to prepare the derivatives characteristic of the compounds of this group. On heating with alkali and aniline, an acid with the empirical formula $C_{13}H_{15}O_3N$ and the anilide of this acid with the empirical formula $C_{19}H_{20}O_2N_2$, were respectively obtained. Reduction of our compound in alcohol with hydrogen in presence of pyrophoric nickel gave α-amino-β-methylvaleric acid (isoleucine). The preparation of these derivatives confirmed our supposition that the product of condensation of methylethyl ketone with hippuric acid with the empirical formula $C_{13}H_{13}O_2N$ is 2-phenyl-4-isobutylidene-5-oxazolone (A).



(A)

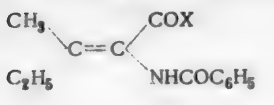
Further investigation of the oxazolone with m.p. 33-37° showed that it is a mixture of two geometrical isomers. Both isomers could be isolated by saponification of the oxazolone with an amount of alkali less than that theoretically required. In these conditions a portion of the product is saponified and goes into solution, while the unsaponified portion remains in the form of an oil which quickly crystallizes when cooled.

Acidification of the alkaline solution with hydrochloric acid causes separation of N-benzoylamino-β-methyl-β-ethylacrylic acid, which on heating with acetic anhydride is converted into 2-phenyl-4-isobutylidene-5-oxazolone with m.p. 52-54°. We designate this isomer (I)

A single crystallization of the crystalline unsaponified residue from alcohol gave a white crystalline compound with m.p. 63-64°. The analysis and properties of this compound corresponded to 2-phenyl-4-isobutylidene-5-oxazolone, which we call isomer (II). The melting point of a mixture of isomers (I) and (II) is 33-37°. More detailed characterization of the prepared isomers appeared of interest. With this objective we plotted the absorption spectra in the ultra-violet region and prepared some derivatives.

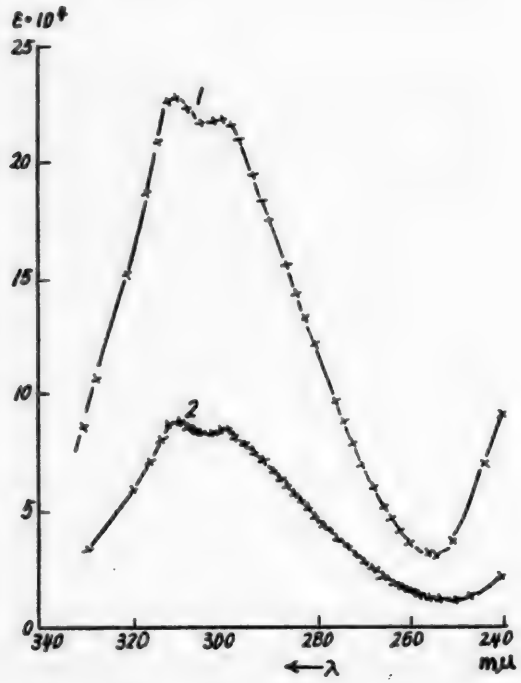
The absorption spectra of isomers (I) and (II) differ in intensity of absorption. The maxima of their spectra are nearly identical (see diagram). Saponification of oxazolones (I) and (II) with alkali yields two isomeric acids (Ia) and (IIa). These acids differ in melting points and in degree of solubility in alcohol; acid (Ia) is soluble in alcohol in the ratio of 1:40, acid (IIa) in the ratio of 1:10. When heated with acetic anhydride the acids revert to their respective oxazolones. When methyl alcohol in presence of a trace of sodium methylate, the oxazolones (I) and (II) form esters of N-benzoylamino-β-methyl-β-ethylacrylic acid (Ib) and (IIb). Treatment with piperidine gives two piperidides of N-benzoylamino-β-methyl-β-ethylacrylic acid, but it was impossible to establish which of these corresponded to oxazolone (I), and which to oxazolone (II). Aniline gave one isomer of the anilide of N-benzoylamino-β-methyl-β-ethylacrylic acid. The formation of only one isomer is evidently due to the ability of geometrical isomers to isomerize in presence of organic bases [3]; on the other hand two isomeric piperidides of the same acid were derived from each geometrical isomer of the oxazolone.

The following geometrical isomers have thus been prepared:



when X = OH geometrical isomers (Ia) and (IIa)
X = OCH_3 " " (Ib) and (IIb)
X = NC_5H_{10} " " (two)
X = NHC_6H_5 " " (one)

In Table 1 are presented the melting points of 2-phenyl-4-isobutylidene-5-oxazolones (I) and (II), and of some of their derivatives.



Ultraviolet absorption spectra of 2-phenyl-4-isobutylidene-5-oxazolone (in alcohol). 1) isomer (I) with m.p. 52-54°; 2) isomer (II) with m.p. 63-64°.

EXPERIMENTAL

1. 2-Phenyl-4-isobutylidene-5-oxazolone (mixture of isomers (I) and (II)). 2-Phenyl-4-isobutylidene-5-oxazolone is prepared by heating methylethyl ketone, hippuric acid, acetic anhydride and sodium acetate [4]. The oxazolone, a dark-red oil, gradually crystallizes on standing. M.p. 33-37°. Yield 60-70 % of the theoretical.

Found %: C 72.43; H 6.07; N 6.56. $C_{13}H_{13}O_2N$. Calculated %: C 72.52; H 6.09; N 6.51.

2. Anilide of N-benzoylamino-β-methyl-β-ethylacrylic acid. 0.75 g 2-phenyl-4-isobutylidene-5-oxazolone (oil), 10 g dry benzene and 0.5 g freshly distilled aniline are heated on a boiling water bath for 30 minutes and then cooled. The crystals are filtered. A further small crop of crystals is got from the mother liquor after distilling off the benzene. The product crystallizes from a mixture of benzene and alcohol (1:2). After three recrystallizations the anilide of N-benzoylamino-β-methyl-β-ethylacrylic acid melts at 254-255°. Yield 70% of theory.

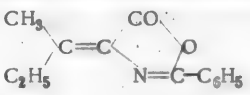
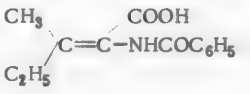
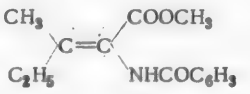
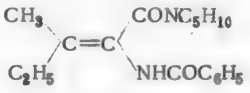
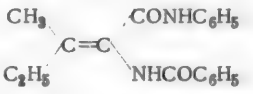
Found %: C 73.79; H 6.61; N 9.04. $C_{19}H_{20}O_2N_2$. Calculated %: C 73.98; H 6.54; N 9.09.

3. N-Benzoylamino-β-methyl-β-ethylacrylic acid (mixture of isomers). 20 g 2-phenyl-4-isobutylidene-5-oxazolone (oil or crystalline isomer with m.p. 33-37°) and 350 ml 2% sodium hydroxide solution are heated for 4 hours; a yellow solution is formed. After cooling, it is shaken with 100 ml ether, the ether is separated and to the remainder is added 10% hydrochloric acid until the reaction is acid to congo. A white crystalline substance comes down and gradually turns pink. It is filtered, washed with a little water and dried. The crystals are then heated with carbon tetrachloride, cooled and filtered. The residue is washed on the filter with a small amount of carbon tetrachloride and dried. The product crystallizes from alcohol with m.p. 198-200°. Yield 55% of theoretical.

Found %: C 66.77; H 6.24; N 6.01. $C_{13}H_{15}O_3N$. Calculated %: C 66.92; H 6.49; N 6.12.

4. α-Amino-β-methylvaleric acid (isoleucine). 20 g 2-phenyl-4-isobutylidene-5-oxazolone is dissolved in 50 ml alcohol; 7 g Raney nickel is added and reduction effected at 70-90° and an initial pressure of 80 atm. Absorption of the requisite amount of hydrogen is complete in 2 hours. At the end of the reaction the mass is filtered and the catalyst well washed with alcohol. The main alcoholic solution and the alcohol washings are combined and distilled to dryness in vacuum. The residue is boiled with 200 ml 17% hydrochloric acid for 7-9 hours. After cooling, the benzoic acid is filtered off. The hydrochloric acid solution is evaporated to dryness in vacuum. Water is twice added to the residue and the evaporation to dryness repeated. The dry residue is dissolved

TABLE 1

Prep. No.	Name	Formula	Melting point of oxazolone (I) and its derivatives	Melting point of oxazolone (II) and its derivatives	Melting point of mixed specimens of the geom. isomers
1	2-Phenyl-4-isobutylidene-5-oxazolone		52-54°	63-64°	33-37°
2	N-Benzoylamino-β-methyl-β-ethylacrylic acid		223-224	200-204	198-200
3	Methyl ester of N-benzoyl-amino-β-methyl-β-ethyl-acrylic acid		155-156	138-139	121-125
4	Piperidide of N-benzoyl-amino-β-methyl-β-ethyl-acrylic acid		141-143	178-179	134-140
5	Anilide of N-benzoyl-amino-β-methyl-β-ethylacrylic acid		254-255°		

The absorption spectra were plotted by Kh. M. Ravikovich to whom we convey our thanks.

in absolute alcohol, addition is made to the solution of diethylamine until the reaction is neutral (bromothymol blue), and the mass is left for 24 hours. It is then filtered and the α-amino-β-methyl-valeric acid is purified by dissolving in water and precipitation with alcohol. M.p. 276-279°. Yield 44% of theoretical.

Found %: C 54.81; H 9.94; N 10.58. $C_6H_{13}O_2N$. Calculated %: C 54.99; H 9.91; N 10.69.

5. 2-Phenyl-4-isobutylidene-5-oxazolone (isomer I). 20 g of the mixture of geometrical isomers (oil) is heated with 125 ml 2% sodium hydroxide solution for 4 hours. A solution and a rapidly crystallizing oily layer are formed. The solution is poured off from the crystals and treated with ether. After removing the ether, the alkaline solution is neutralized with 10% hydrochloric acid. The white precipitate is filtered off and heated with carbon tetrachloride. After filtering, the precipitate is crystallized three times from alcohol. N-Benzoylamino-β-methyl-β-ethylacrylic acid (Ia) melts at 223-224°. The acid is insoluble in water, poorly soluble in cold alcohol, and soluble in hot alcohol in the ratio of 1:40. 5 g N-benzoylamino-β-methyl-β-ethylacrylic acid is heated on the boiling water bath for 20 minutes with 25 ml acetic anhydride. On cooling, the acetic anhydride is distilled off in vacuum. The residue is crystallized from alcohol. M.p. of the oxazolone (I) 52-54°. Yield 70-75%.

Found %: C 72.35; H 6.04; N 6.31. $C_{13}H_{13}O_2N$. Calculated %: C 72.52; H 6.09; N 6.51.

6. Methyl ester of N-benzoylamino-β-methyl-β-ethylacrylic acid (isomer Ib). 1 g 2-phenyl-4-isobutylidene-5-oxazolone (I) is dissolved in 100 ml absolute methyl alcohol to which is added 4 mg metallic sodium, and left for 20-25 hours. The alcohol is then distilled off in vacuum to half the volume, neutralization is cautiously effected with a drop of hydrochloric acid and another portion of the alcohol is distilled off. The methyl ester of N-benzoylamino-β-methyl-β-ethylacrylic acid (Ib) is recrystallized from alcohol as white lustrous crystals. M.p. 155-156°.

Found %: C 67.85; H 6.88; N 5.45. $C_{14}H_{17}O_3N$. Calculated %: C 67.99; H 6.94; N 5.66.

7. 2-Phenyl-4-isobutylidene-5-oxazolone (isomer II). Heating of the mixture of geometrical isomers with alkali gives an alkaline solution and a crystalline yellowish-red substance (expt. 5). The crystalline substance is recrystallized several times from 70% alcohol; oxazolone (II) separates in the form of white needles with m.p. 63-64°.

Found %: C 72.30; H 5.83; N 6.45. $C_{13}H_{13}O_2N$. Calculated %: C 72.52; H 6.09; N 6.51. A mixed sample with isomer (I) melts at 33-37°. Heating of oxazolone (II) with 2% sodium hydroxide solution for $1\frac{1}{2}$ hrs gives N-bebzoylamino-β-methyl-β-ethylacrylic acid with m.p. 202-204° (isomer IIa).

Found %: C 67.03; H 6.71; N 5.87; M 235.6. $C_{13}H_{15}O_3N$. Calculated %: C 66.92; H 6.49; N 6.01; M 233.12. A mixed sample with the isomeric acid (Ia) melts at 198-200°. Acid (IIa) changes into the oxazolone (II) when heated with acetic anhydride.

8. Methyl ester of N-benzoylamino-β-methyl-β-ethylacrylic acid (isomer IIb). This ester is prepared from oxazolone (II) in the same manner as from oxazolone (I) (expt.6). M.p. 138-139°.

Found %: C 67.92; H 6.88; N 5.94. $C_{14}H_{17}O_3N$. Calculated %: C 67.99; H 6.94; N 5.66.

A mixture of esters (Ib and IIb) melts at 121-123°.

9. Piperidides of N-benzoylamino-β-methyl-β-ethylacrylic acid. 0.85 g 2-phenyl-4-isobutylidene-5-oxazolone (isomer I or II), 5 ml dry benzene and 1 ml piperidine are heated on the boiling water bath for 1 hour. The benzene is then distilled off in vacuum. The residue is triturated with 5 ml dry ether and filtered. The precipitate is twice crystallized from alcohol. M.p. 141-143°.

Found %: C 71.69; H 7.78; N 9.55. $C_{18}H_{24}O_2N_2$. Calculated %: C 71.95; H 8.06; N 9.33. Removal of the ether from the ethereal mother liquor yields a crystalline substance. After 2 or 3 crystallizations from alcohol it melts at 178-179°.

Found %: C 72.26; H 8.10; N 9.50. $C_{18}H_{24}O_2N_2$. Calculated %: C 71.95; H 8.06; N 9.33. A mixture of the two piperidides melts at 134-140°.

SUMMARY

1. It is shown that methylethyl ketone reacts with hippuric acid to form 2-phenyl-4-isobutylidene-5-oxazolone (A).

2. The compound with m.p. 33-37° is shown to be a mixture of two geometrical isomers (I) and (II). The isomers were separated and some of their derivatives prepared.

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Received April 24, 1951

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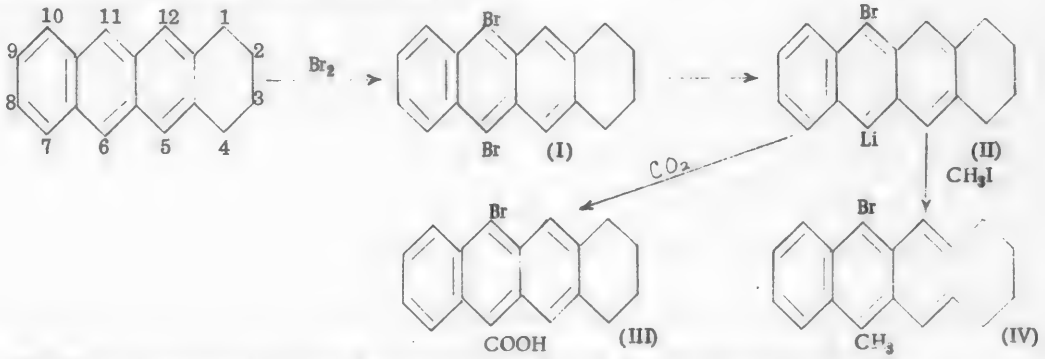
INVESTIGATIONS IN THE NAPHTHACENE SERIES

II. ORGANOLITHIUM COMPOUNDS OF 1,2,3,4-TETRAHYDRONAPHTHACENE AND THEIR TRANSFORMATIONS [1]

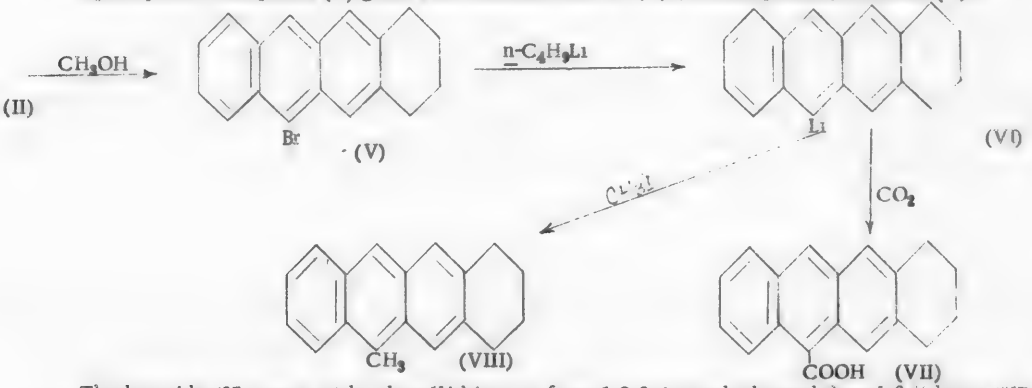
B. M. Mikhailov and A. D. Chinaeva

We have shown that the method of preparation of organolithium compounds consisting in reacting n-butyllithium or phenyllithium with aryl bromides can be successfully applied to a series of polynuclear condensed hydrocarbons — anthracene [2], 1,2-benzanthracene [3] and phenanthrene [4].

In this communication we describe the preparation by this method of organolithium compounds of 1,2,3,4-tetrahydronaphthacene and their transformations leading to the synthesis of derivatives of the linear tetracyclic hydrocarbon. The starting material for this investigation was 6,11-dibrom-1,2,3,4-tetrahydronaphthacene (I), which is readily prepared by the action of two equivalents of bromine on 1,2,3,4-tetrahydronaphthacene. Reaction of phenyllithium with the dibromide of 1,2,3,4-tetrahydronaphthacene gives 6-bromo-1,2,3,4-tetrahydronaphthacyl-11-lithium (II). Compound (II) is converted by carboxylation into 11-bromo-1,2,3,4-tetrahydronaphthacene-6-carboxylic acid (III); reaction of the organo-metallic compound (II) with methyl iodide leads to formation of 11-bromo-6-methyl-1,2,3,4-tetrahydronaphthacene (IV):



Hydrolysis of compound (II) gives the monobromide of 1,2,3,4-tetrahydronaphthacene (V):



The bromide (V) reacts with n-butyllithium to form 1,2,3,4-tetrahydronaphthacyl-6-lithium (VI), which by treatment with CO_2 is converted into 1,2,3,4-tetrahydronaphthacene-6-carboxylic acid (VII); with methyl iodide it gives 6-methyl-1,2,3,4-tetrahydronaphthacene (VIII).

Replacement of halogen by lithium can also be readily effected by the same method in 11-bromo-6-methyl-

1,2,3,4-tetrahydronaphthacene (IV). The resultant organolithium compound reacts with methyl iodide to form 6,11-dimethyl-1,2,3,4-tetrahydronaphthacene (IX):

EXPERIMENTAL

All the operations with organolithium compounds were performed at atmospheric pressure.

6,11-Dibromo-1,2,3,4-tetrahydronaphthacene (I). To a cooled (to 0°) suspension of 7.5 g 1,2,3,4-tetrahydronaphthacene [1] in 375 ml carbon tetrachloride, placed in a three-necked flask fitted with dropping funnel, stirrer and reflux condenser, was added dropwise with stirring over a period of 40 minutes 12 g bromine diluted with 60 ml carbon tetrachloride. With progressive addition of bromine the 1,2,3,4-tetrahydronaphthacene went into solution and hydrogen bromide was evolved. After heating for 20 minutes on a water bath, the brown reaction mixture was filtered, the solvent distilled off and the residue recrystallized from benzene and then from chloroform-alcohol mixture. Yield 8.25 g 6,11-dibromo-1,2,3,4-tetrahydronaphthacene with m.p. 186-188°. The yield was equivalent to 65.4% of the theoretical.

The compound forms dark-yellow rhombic platelets, readily soluble in chloroform and benzene, poorly soluble in alcohol and ether.

7.252 mg substance: 14.659 mg CO_2; 2.312 mg H_2O. Found %: C 55.16; H 3.56. $C_{18}H_{14}Br_2$. Calculated %: C 55.39; H 3.61.

11-Bromo-1,2,3,4-tetrahydronaphthacene-6-carboxylic acid (III). To a solution in ether of phenyllithium (0.0012 mole) in a two-limbed ampoule is added a benzene solution of 0.5 g 6,11-dibromo-1,2,3,4-tetrahydronaphthacene (0.0012 mole). The transparent reaction mixture is left for 1½ hours at room temperature and then poured onto solid carbon dioxide. After evaporation of the carbon dioxide, water is added. The aqueous layer is separated and acidified with dilute hydrochloric acid. The precipitated acid is filtered off, washed, and twice crystallized from methanol to give 0.15 g acid (32.6%) in the form of yellow needles with m.p. 227° (with decomp). The acid is readily soluble in ethanol, poorly in methanol.

6.587 mg substance: 15.532 mg CO_2; 2.548 mg H_2O. Found %: C 64.34; H 4.32. $C_{19}H_{15}O_2Br$. Calculated %: C 64.22; H 4.26.

6-Methyl-11-bromo-1,2,3,4-tetrahydronaphthacene (IV). A benzene solution (40 ml) of 2 g 6,11-dibromo-1,2,3,4-tetrahydronaphthacene (0.0051 mole) is added to an ethereal solution of phenyllithium (0.0103 mole). To the brown reaction mixture, after standing for an hour at room temperature, is added 2.3 g methyl iodide diluted with ether. The reaction mixture (now lighter in color) is left for an hour at room temperature and then washed with water. The residue obtained after distilling off the solvent is purified by crystallization from chloroform-alcohol mixture, petroleum ether, and finally acetone. There was obtained 0.9 g 6-methyl-11-bromo-1,2,3,4-tetrahydronaphthacene in the form of prisms melting at 135-136° (with decomp). Yield 54% of the theoretical. After further crystallization from benzene-acetone the substance (0.7 g) had m.p. 144-146°. It is readily soluble in benzene and chloroform, poorly in alcohol, petroleum ether, acetone and ethyl acetate.

5.468 mg substance: 14.010 mg CO_2; 2.658 mg H_2O. Found %: C 69.99; H 5.47. $C_{19}H_{17}Br$. Calculated %: C 70.15; H 5.27.

6-Bromo-1,2,3,4-tetrahydronaphthacene (V). 3 g 6,11-dibromo-1,2,3,4-tetrahydronaphthacene was dissolved in a mixture of 40 ml benzene and 20 ml ether. To the solution, in a flask with a two-branch adaptor, was run from an ampoule a solution of n-butyllithium prepared from 1.09 g n-butyl chloride, 0.16 g lithium and 5 ml ether. After 30 minutes the reaction mass, which contained a precipitate of organometallic compound, was hydrolyzed with an ethereal solution of methanol. The ether-benzene solution was washed with water and the solvent distilled off. The residue was crystallized from chloroform-methanol and then from acetone, giving 0.75 g of substance with m.p. 107-110°; a second fraction of 0.52 g with m.p. 103-105° was isolated from the mother liquor. Yield 53%. After recrystallization from benzene-methanol and chloroform-methanol, the substance formed long needles with m.p. 110-111°. Readily soluble in chloroform and benzene, not so soluble in alcohol and petroleum ether.

5.590 mg substance: 14.304 mg CO_2; 2.524 mg H_2O. Found %: C 69.83; H 5.05. $C_{19}H_{15}Br$. Calculated %: C 69.46; H 4.85.

1,2,3,4-Tetrahydronaphthacene-6-carboxylic acid (VII). A benzene solution of 1 g 6-bromo-1,2,3,4-tetrahydronaphthacene (10 ml) was run into an ampoule containing n-butyllithium prepared from 0.62 g n-butyl chloride, 0.094 g lithium and 10 ml ether. After standing at room temperature for 30 minutes the reaction mass was poured onto solid carbon dioxide; when water was added a precipitate appeared at the boundary between the water and ether layers, consisting of 1,2,3,4-tetrahydronaphthacene (0.3 g). Acidification of the aqueous layer gave acid (VII) which was purified by reprecipitation from sodium carbonate solution, followed by recrystallization from glacial acetic acid. Yield 0.2 g (22.5% of acid with m.p. 195-196°)

4.296 mg substance: 12.972 mg CO_2; 2.390 mg H_2O. Found %: C 82.40; H 6.22. $C_{19}H_{16}O_2$. Calculated %: C 82.58; H 5.83.

6-Methyl-1,2,3,4-tetrahydronaphthacene (VIII). n-Butyllithium was prepared from 0.126 g lithium, 1.63 g n-butyl chloride and 10 ml ether. To the ethereal solution of n-butyllithium was added a benzene solution of 2 g 6-bromo-1,2,3,4-tetrahydronaphthacene (20 ml), whereupon the solution became considerably lighter in color. After standing for 30 minutes at room temperature, addition was made to the reaction mixture of 4.5 g methyl iodide diluted with 10 ml ether, and the mixture was again left at room temperature for an hour. The benzene-ether solution was washed with water and the solvents driven off. The yellow crystalline precipitate was crystallized from acetone to give 1.1 g (70%) of substance with m.p. 123-124.5°. After recrystallization from acetone, white needles were obtained with m.p. 127-128°. The hydrocarbon dissolves readily in carbon tetrachloride and chloroform, not so readily in acetone and ether.

4.110 mg substance: 13.951 mg CO_2; 2.763 mg H_2O. Found %: C 92.63; H 7.52. $C_{19}H_{18}$. Calculated %: C 92.63; H 7.36.

6,11-Dimethyl-1,2,3,4-tetrahydronaphthacene (IX). Into an ampoule containing a solution of n-butyllithium prepared from 0.05 g lithium and 0.3 g n-butyl chloride, was introduced 10 ml of a benzene solution of 0.7 g 6-methyl-11-bromo-1,2,3,4-tetrahydronaphthacene (m.p. 143-144°). The transparent brown reaction mixture was stood for an hour at room temperature. Addition of an ethereal solution of 1.2 g methyl iodide generated heat and the color changed to yellow. After standing for 40 minutes at room temperature, the ether-benzene solution was washed with water and the solvents distilled off. The yellow crystalline residue was crystallized from benzene-alcohol, giving 0.35 g 6,11-dimethyl-1,2,3,4-tetrahydronaphthacene with m.p. 139-142° (yield 62.5% of theory). After a second crystallization from benzene-alcohol the m.p. was 142-143.5°. 6,11-Dimethyl-1,2,3,4-tetrahydronaphthacene is readily soluble in benzene and chloroform and not so soluble in alcohol and acetone. It crystallizes from benzene in the form of elongated yellow platelets.

3.774 mg substance: 12.780 mg CO_2; 2.553 mg H_2O. Found %: C 92.41; H 7.57. $C_{20}H_{20}$. Calculated %: C 92.25; H 7.75.

The microanalyses were performed in our laboratory by assistant N. M. Krauze.

SUMMARY

1. n-Butyllithium or phenyllithium acts on 6,11-dibromo-, 6-methyl-11-bromo-, and 6-bromo-1,2,3,4-tetrahydronaphthacenes to form the corresponding organolithium compounds of 1,2,3,4-tetrahydronaphthacene.

2. A series of derivatives of 1,2,3,4-tetrahydronaphthacene was prepared with the help of organolithium compounds.

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Received February 21, 1951

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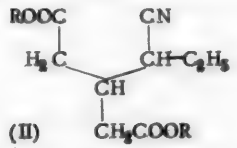
* See Consultants Bureau translation, p. 203.

** See Consultants Bureau translation, p. 1659.

VI. SYNTHESIS OF γ-ETHYL-δ-VALEROLACTONE-β-ACETIC AND β-(α'-BROMOMETHO)-PROPYLGLUTARIC ACIDS

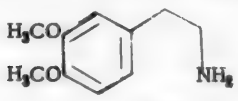
L. I. Zakharkin and N. A. Preobrazhensky

In carrying out our synthesis of the alkaloid emetine [1] (I) it was necessary to prepare a starting substance whose structure corresponded to the middle portion of the molecule of the alkaloid. For this purpose we have previously made successful use of an ester of β-(α'-cyano)-propylglutaric acid (II).



(II)

We found that the same objective is achieved satisfactorily by using γ-ethyl-δ-valerolactone-acetic acid (III) and the β-(α'-bromometho)-propylglutaric acid (IV) derived therefrom. Condensation of these compounds (III) and (IV) with homoveratrylamine (V), leads via a series of intermediate stages to emetine (I).



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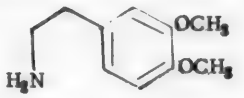

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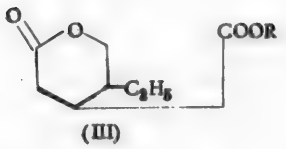
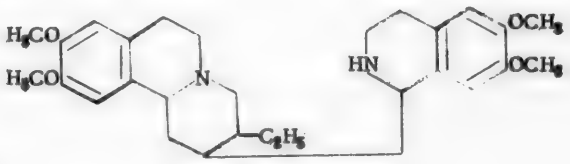
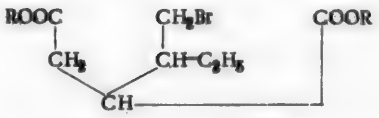


(III)

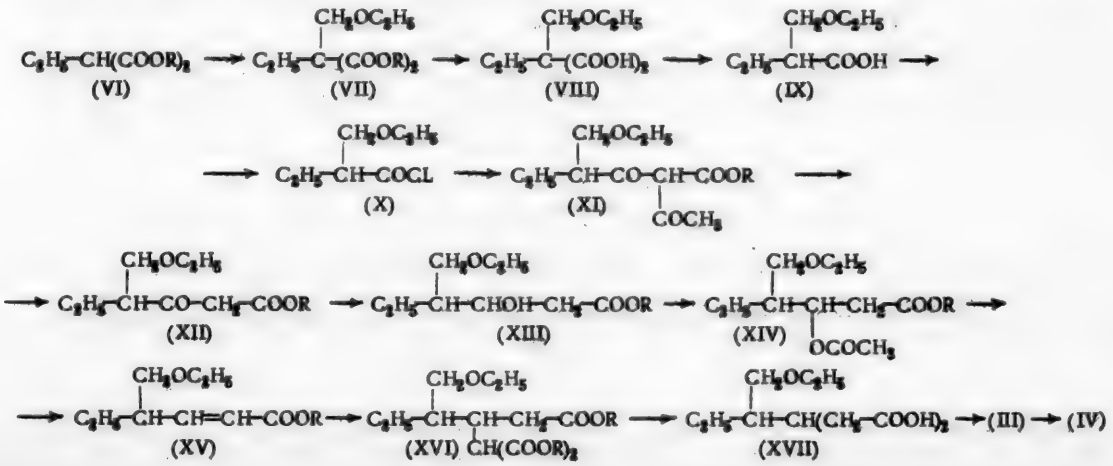


(I)

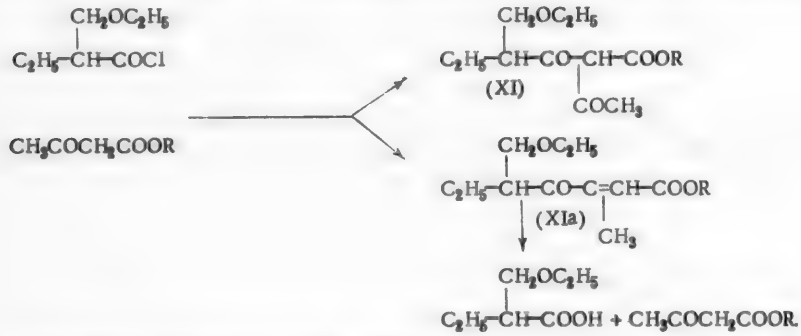


(IV)

The synthesis of γ-ethyl-δ-valerolactone-β-acetic acid (III) and of β-(α'-bromometho)-propylglutaric acid (IV) was effected according to the following scheme:

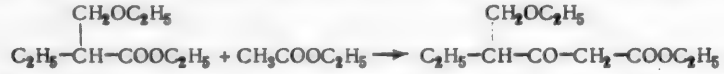


The ethyl ester of ethylmalonic acid (VI) is condensed with chloromethylethyl ether and the resultant ethoxymethylethylmalonic ester (VII) is saponified with alcoholic potash to give the dicarboxylic acid (VIII). Decarboxylation of the latter leads to α-ethoxymethylbutyric acid (IX). An interesting feature is the simultaneous formation of ethacrylic acid. The acid chloride (X) is condensed with sodium ethylacetoacetate and from the resultant mixture of isomeric acyl derivatives (XI) and (XIa) the ethyl ester of α-aceto-β-keto-γ-ethoxymethylcaproic acid (XI) is isolated by extraction with cold dilute potassium hydroxide solution. Saponification of the acyl derivative (XIa) with sodium hydroxide gives the original γ-ethoxymethylbutyric acid:



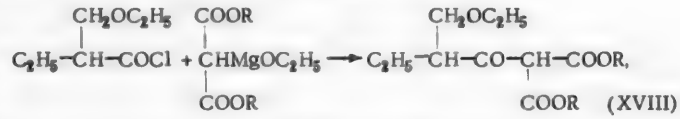
Treatment of compound (XI) with dry ammonia in ether solution yields the ester of β-keto-γ-ethoxymethylcaproic acid (XII).

Other routes to the ethyl ester of β-keto-γ-ethoxymethylcaproic acid were also investigated, avoiding the step of condensation of α-ethoxymethylbutyryl chloride with sodium ethylacetoacetate since the yield of the required acyl derivative (XI) does not exceed 50% of theory. For this purpose the ethyl ester of α-ethoxymethylbutyric acid was prepared and condensed in presence of sodium alcoholate with ethyl acetate:



In view of the poor yields, however, this method was abandoned.

Similarly it was impossible to utilize the condensation of α-ethoxymethylbutyryl chloride with ethyl magnesium malonate which is effected with good yield:



because difficulties arise in the subsequent cleavage of the α-carboxy group by heating with a naphthalene sulfonic acid [2].

The compound (XII) is converted into the sought for substance by the following steps: The ethyl ester (XII) is catalytically reduced to the corresponding hydroxy derivative (XIII) which is then dehydrated to the unsaturated ester (XV). We examined various methods of dehydrating the ethyl ester of β-hydroxy-γ-ethoxymethylcaproic acid (XIII) since methods of dehydration of esters of β-hydroxy acids have been developed mainly for compounds in which the hydroxy group is at a tertiary carbon atom [3] (products of condensation of ketones with an ester of α-bromoacids by the Reformatsky reaction). Dehydration of esters of β-hydroxy acids with the hydroxy group at a secondary carbon atom has not been so closely investigated because usually in this case the corresponding esters of the unsaturated acids are readily prepared by condensation of aldehydes with malonic acid or a monoester of malonic acid.

Dehydration of the ethyl ester of β-hydroxy-γ-ethoxymethylcaproic acid proceeded with low yields by the usual methods, using phosphorus pentoxide, thionyl chloride in presence of pyridine, distillation with potassium carbonate or with potassium hydrogen sulfate. The unsaturated compound was also impure. We found that better results could be obtained in the dehydration reaction if the hydroxy compound (XIII) was first converted into the corresponding acetyl derivative (XIV). Acetic acid is readily split off from the latter (by heating with fused potassium acetate), and the unsaturated ester (XV) is formed. Condensation of the latter with sodium ethyl

malonate gives the tricarboxylic acid ester (XVI) which is converted by saponification and decarboxylation into β-(α'-ethoxymethopropylglutaric acid (XVII). Heating of the latter with 48% hydrobromic acid gives γ-ethyl-δ-valerolactone-β-acetic acid (III) which we isolated in both a liquid and a crystalline form. Both these forms react with dry hydrogen bromide to form β-(α'-brommetho)-propylglutaric acid.

EXPERIMENTAL

1. Diethyl ester of ethoxymethylethylmalonic acid (VII). To 12 g finely divided sodium under 200 ml dry benzene is added 1 ml absolute alcohol and then, gradually, 94 g ethylmalonic ester. After the sodium had dissolved, the reaction mass is cooled and gradual addition made with energetic stirring of 50 g chlormethylethyl ether at such a rate that the temperature does not rise above +2°. The stirrer is then stopped and the mass allowed to stand overnight. On the following day the mixture is heated with stirring at 60-65° for 20 minutes. After cooling, water is added to dissolve the sodium chloride and the benzene layer is separated and washed with soda solution. The benzene is distilled off in vacuum. The diethyl ester of ethoxymethylethylmalonic acid has b.p. 114-117° at 9 mm. Yield 94 g or 76.5% of the theoretical.

2. Ethoxymethylethylmalonic acid (VIII). To a solution of 75 g potassium hydroxide in 300 ml methyl alcohol is added 111 g diethyl ester of ethoxymethylethylmalonic acid and the mixture agitated until the latter dissolves. The solution is stood overnight and on the next day it is heated on the water bath to the boiling point of the alcohol for two hours. Addition is then made of 150 ml water to dissolve the potassium salt and the methyl alcohol is taken off in vacuum. The residual transparent aqueous solution is acidified with concentrated hydrochloric acid and extracted several times with ether. After removing the solvent, the residue crystallizes. Yield 83 g (97.5%). M.p. 69-70° after recrystallization from benzene-ligroin.

3.010 mg substance: 5.570 mg CO_2; 1.950 mg H_2O. Found %: C 50.50; H 7.25. $C_8H_{14}O_5$. Calculated %: C 50.50; H 7.42.

3. α-Ethoxymethylbutyric acid (IX). 80 g of ethoxymethylethylmalonic acid is heated on an oil bath at 155-160° for 40 minutes until carbon dioxide ceases to come off. The product is then fractionated in vacuum. B.p. 113-115° at 9 mm. Yield 42.5 g (69% of theory); n_D^{10} 1.4278.

2.995 mg substance: 6.305 mg CO_2; 2.605 mg H_2O. Found %: C 57.45; H 9.73. $C_7H_{14}O_3$. Calculated %: C 57.50; H 9.65.

The first fraction yielded 10 g α-ethacrylic acid with b.p. 178-180°.

4. α-Ethoxymethylbutyryl chloride (X). 45 g α-ethoxymethylbutyric acid is mixed with 50 g thionyl chloride and left overnight. The mixture is then heated on the water bath for an hour. The excess of thionyl chloride is distilled off and the acid chloride distilled in vacuum. B.p. of the acid chloride 57-58° at 8 mm. Yield 47 g (92.5% of theory).

5. Ethyl ester of α-carbethoxy-β-oxo-γ-ethoxymethylcaproic acid (XVIII). To 2.5 g magnesium turnings, 2.5 ml absolute alcohol, and 0.1 ml carbon tetrachloride is gradually added a mixture of 16 g ethyl malonate and 3 ml absolute alcohol. The reaction of formation of the magnesium compounds proceeds energetically and cooling is necessary at the start. After the reaction has slowed down, addition is made to the flask of 30 ml dry ether, and the flask is heated on the water bath until the whole of the magnesium has dissolved. Slow addition is then made to the ethyl magnesium malonate of a solution of 17 g α-ethoxymethylbutyryl chloride in 20 ml dry ether at such a speed that the ether boils. After all has been added, the transparent ethereal solution is heated on the water bath for an hour. After cooling with ice water, addition is made to the reaction mass of 30 ml water and then of dilute hydrochloric acid in amount necessary to dissolve the magnesium compounds. The ethereal solution is washed once with water and dried with sodium sulfate. The residue (after removal of solvent) is distilled in vacuum. B.p. 143-145° at 6 mm. Yield 21 g (73%). A dark-red solution is formed with an alcoholic solution of iron chloride: n_D^{20} 1.4511.

3.465 mg substance: 7.435 mg CO_2; 2.635 mg H_2O. Found %: C 58.55; H 8.51. $C_{14}H_{24}O_6$. Calculated %: C 58.30; H 8.39.

6. Ethyl ester of α-aceto-β-keto-γ-ethoxymethylcaproic acid (XI). Sodium ethylacetoacetate is prepared from 4.8 g sodium and 28 g ethylacetoacetate in 150 ml absolute ether. Gradual addition is made to it, with stirring and cooling to −5 to 3° of 33 g α-ethoxymethylbutyryl chloride. Stirring is then continued for an hour, after which the reaction mass is heated on the water bath for 30 minutes. Water is added

to dissolve the sodium chloride. The ether solution is washed once with water and dried with calcined sodium sulfate. The ether is distilled off on the water bath and the residue cooled with ice-salt mixture and extracted with cold 7% potassium hydroxide solution until the whole of the acyl derivative has been extracted. The alkaline solution is extracted once with ether and the cooled residue is acidified with dilute hydrochloric acid. The separated oil is extracted with ether and the ether extract washed several times with bicarbonate solution. After drying with sodium sulfate, the ether is distilled off and the residue distilled in vacuum. B.p. 130-132° at 9 mm. Yield 24.2 g (46.5% of theory); n_D^{20} 1.4691.

3.000 mg substance; 6.665 mg CO_2; 2.340 mg H_2O. Found %: C 60.54; H 8.73. $C_{13}H_{22}O_5$. Calculated %: C 60.43; H 8.59.

7. Ethyl ester of β-keto-γ-ethoxymethylcaproic acid (XII). 38 g ethyl ester of α-aceto-β-keto-γ-ethoxymethylcaproic acid is dissolved in 60 ml dry ether. A stream of dry ammonia is passed through the solution (cooled to 0°). After complete saturation with ammonia, the solution is left overnight. Water is then added to dissolve the precipitated acetamide. The ether solution is washed with dilute hydrochloric acid and water. After drying with sodium sulfate, the ether is distilled off and the residue distilled in vacuum. B.p. 115-117° at 8 mm. Yield 27 g (83.5% of theory); n_D^{20} 1.4395.

3.450 mg substance; 7.740 mg CO_2; 2.790 mg H_2O. Found %: C 61.22; H 9.05. $C_{11}H_{20}O_4$. Calculated %: C 61.07; H 9.33.

8. Ethyl ester of β-hydroxy-γ-ethoxymethylcaproic acid (XIII). 27 g ethyl ester of β-keto-γ-ethoxymethylcaproic acid, 30 ml absolute alchol and 6 g nickel catalyst are charged into an autoclave and hydrogenation is carried out at 125-130° and 150-160 atm for two hours. The alcoholic solution is freed from catalyst, the alcohol distilled off on the water bath and the residue distilled in vacuum. B.p. 120-121° at 8 mm. Yield 26 g (95.3%); n_D^{20} 1.4395.

2.995 mg substance: 6.545 mg CO_2; 2.730 mg H_2O. Found %: C 60.44; H 10.34. $C_{11}H_{22}O_4$. Calculated %: C 60.50; H 10.16.

9. Ethyl ester of β-acetoxy-γ-ethoxymethylcaproic acid (XIV). 26 g ethyl ester of β-hydroxy-γ-ethoxymethylcaproic acid is heated on the oil bath with 39 ml acetic anhydride for an hour. The acetic acid and excess of acetic anhydride are removed in vacuum. B.p. 131-133° at 9 mm. Yield 30.2 g (97.4% of theory); n_D^{20} 1.4337.

3.064 mg substance: 6.760 mg CO_2; 2.500 mg H_2O. Found %: C 60.19; H 9.13. $C_{13}H_{24}O_5$. Calculated %: C 59.96; H 9.30.

10. Ethyl ester of γ-ethyl-γ-ethoxymethylcrotonic acid (XV). 30.2 g ethyl ester of β-acetoxy-γ-ethoxymethylcaproic acid and 1.5 g fused potassium acetate are heated on a gauze. Acetic acid distils off (the temperature must not exceed 150-155°). When this stage is completed, the mass is cooled and water is added to dissolve the potassium acetate. The oil is extracted with ether. From the distillate, after neutralization, is obtained another crop of substance. The ethereal solution is washed with sodium bicarbonate solution and with water. After drying with sodium sulfate, the ether is driven off and the residue distilled in vacuum. B.p. 103-106° at 9 mm. Yield 20.1 g (86.5%); n_D^{20} 1.4465.

3.095 mg substance: 7.510 mg CO_2; 2.785 mg H_2O. Found %: C 66.22; H 10.07. $C_{11}H_{20}O_3$. Calculated %: C 65.95; H 10.07.

11. Diethyl ester of α-carbethoxy-β-(α'-ethoxymetho)-propylglutaric acid (XVI) 2.3 g sodium is dissolved in 40 ml absolute alcohol and after cooling addition is made of 32 g ethyl malonate. The mixture is heated to the boil on the water bath and addition is gradually made of 20 g ethyl ester of γ-ethyl-γ-ethoxymethylcrotonic acid. The solution is heated on the water bath for 6 hours, after which the alcohol is removed in vacuum. The residue is cooled, addition is made of 70 ml benzene and of dilute hydrochloric acid until the reaction is acid to congo. The benzene solution is separated from the aqueous layer and washed several times with sodium bicarbonate solution until the aqueous extracts are colorless. The benzene is removed in vacuum. B.p. 146-148° at 2 mm. Yield 28.5 g (79% of the theoretical); n_D^{20} 1.4519.

3.000 mg substance: 6.600 mg CO_2; 2.310 mg H_2O. Found %: C 60.04; H 8.62. $C_{18}H_{32}O_7$. Calculated %: C 59.96; H 8.95.

12. β-(α'-Ethoxymetho)-propylglutaric acid (XVII). To a solution of 12.6 g potassium hydroxide in

80 ml water and 160 ml methyl alcohol is added 27 g diethyl ester of β-carbethoxy-β-(α'-ethoxymetho)-propylglutaric acid. The mixture is heated on the water bath for three hours. Water is then added and the methyl alcohol distilled off in vacuum. The aqueous solution is acidified with concentrated hydrochloric acid and extracted several times with ether. The ether is removed on the water bath and the residue heated on an oil bath at 155-160° for 40 minutes until carbon dioxide ceases to come off. There is obtained 16.5 g (95%) of β-(α'-ethoxymetho)-propylglutaric acid with m.p. 190-194° at 3 mm. The acid is a colorless, viscous oil.

2.945 mg substance: 6.150 mg CO_2; 2.240 mg H_2O. Found %: C 56.99; H 8.51. $C_{11}H_{20}O_5$. Calculated %: C 56.86; H 8.68.

13. γ-Ethyl-δ-valerolactone-β-acetic acid (III). 25 g β-(α'-ethoxymetho)-propylglutaric acid is dissolved in 250 g 48% hydrobromic acid and the solution heated at the boil for 6 hours. The hydrobromic acid is then driven off by heating on a water bath in vacuum. To the viscous residue is added 50 ml water and the solution extracted several times with ether. The ether is distilled off and the residue distilled in vacuum. B.p. 170-173° at 3 mm. Yield 16.3 g (81.5%). After standing for a short period the oily product crystallizes, giving 5.65 crystalline acid. Both these substances are lactones of one and the same composition, judging by the analytical and titration data. The melting point of crystalline γ-ethyl-δ-valerolactone-β-acetic acid after recrystallization from benzene is 102.5-103.5°.

a) Crystalline acid. 3.000 mg substance: 6.410 mg CO_2; 1.955 mg H_2O. Found %: C 58.31; H 7.29. $C_9H_{14}O_4$. Calculated %: C 58.03; H 7.58.

Neutralization of 0.2012 g substance in the cold required 12.2 ml 0.0891 N NaOH; after boiling with excess alkali the consumption was 24.3 ml 0.0891 N NaOH. Found: M 185, 92.7. $C_9H_{14}O_4$. Calculated: M 186, 93.0.

b) Liquid acid. 3.600 mg substance: 7.655 mg CO_2; 2.375 mg H_2O. Found %: C 58.03; H 7.38. $C_9H_{14}O_4$. Calculated %: C 58.03; H 7.58.

Neutralization of 0.1436 g substance in the cold consumed 8.7 mg 0.0891 N NaOH; after boiling with excess alkali the consumption was 17.4 ml 0.0891 N NaOH. Found: M 185.5, 92.7. $C_9H_{14}O_4$. Calculated: M 186.0, 93.0.

14. β-(α'-Bromometho)-propylglutaric acid (IV). A solution of 5 g γ-ethyl-δ-valerolactone-β-acetic acid in 50 ml glacial acetic acid is saturated with dry hydrogen bromide at 0° and left for 48 hours. The acetic acid is then distilled off in vacuum at 40° on the water bath. The residue is dissolved in benzene and the benzene distilled off in vacuum. A small quantity of ether is added; after a short period the mass thickens due to separation of crystals. The crystals are collected on a filter and washed with a little benzene. Yield 3.2 g (44.6%). M.p. 132.5-133.5° after recrystallization from benzene.

2.835 mg substance: 4.220 mg CO_2; 1.455 mg H_2O. Found %: C 40.62; H 5.74. $C_9H_{15}O_4Br$. Calculated %: C 40.44; H 5.66.

SUMMARY

A method is developed for the preparation of γ-ethyl-δ-valerolactone-β-acetic acid and the ester of β-(α'-bromometho)-propylglutaric acid, starting materials for the synthesis of emetine.

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Received March 31, 1951

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PREPARATION OF 3,4-DIMETHYLPHENYL-d-RIBAMINE

BY THE REARRANGEMENT METHOD

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3,4-Dimethylphenyl-d-ribamine is an intermediate in the synthesis of vitamin B_2, riboflavin. It can be easily prepared by condensation of 3,4-dimethylaniline with d-ribose. But d-ribose is not a readily accessible substance, so that great interest has developed in methods of synthesis of this interemediate from more accessible starting products, in particular from d-arabinose.

The structure of the glucosoanilides has been discussed ever since their discovery [1,2,3]. Sorokin and Marshevsky [4] investigated the hexose anilides and ascribed to the reaction products a glucoside structure characterized by a γ-bond:

$$HOCH_2-CHOH-CH-CHOH-CHOH-CH-NHC_6H_5$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

Schiff [5] and Straus [6] favored the aminoaldehyde formula. They claimed that reaction of a sugar with an amine leads to Schiff bases $-HOCH_2-(CHOH)_4-CH{=}NC_6H_5$. Irvine and co-workers [7] inclined to the N-glucoside formula.

Arylamino-N-glucosides are prepared by heating a sugar with an amine without a solvent or with a solvent (alcohol, water, benzene). Partial removal of the solvent causes the N-glucosides to crystallize. A catalyst was needed for the formation of some N-glucosides (NH_4Cl, HCl, etc.) [8].

The majority of the N-glucosides remain unchanged only in the absolutely pure state. Marked changes are caused by the presence of traces of impurities.

Amadori [9] showed that fusion, and also prolonged digestion, of amines with sugars leads to formation, not of N-glucosides, but of their isomers. Kuhn and Wygand [10] obtained p-tolyl-d-isoglucosamine from p-toluidine and d-glucose.

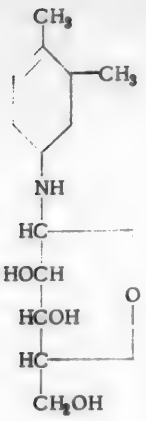
Following a detailed study of the conditions of rearrangement for derivatives of hexoses, the possibility of rearrangement of N-pentosides was investigated.

Of particular interest in connection with the synthesis of vitamin B_2 is the coupling of d-arabinose with 3,4-dimethylaniline, since their interaction followed by rearrangement and hydrogenation gives 3,4-dimethylphenyl-d-ribamine. Condensation of 3,4-dimethylaniline with d-arabinose leads to formation of 3,4-dimethylphenyl-d-arabinoside (I), which, when heated in an acid medium, rearranges to 3,4-dimethylphenyl-d-isoarabinosamine (II); reduction of the latter by hydrogen in presence of platinum in a weakly alkaline medium gives 3,4-dimethylphenyl-d-ribamine (III). During the reaction d-isoarabinosamine was not isolated in the free state. Berezovsky, Kurdyukova and Preobrazhensky [12], using a platinum catalyst, prepared d-ribosamine from d-arabinose in a yield of about 13 % of the theoretical. (For diagram see next page)

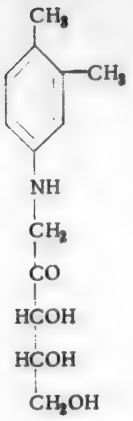
The present investigation was undertaken because of the need to raise the yield of d-ribamine and to replace the platinum catalyst by the cheaper nickel catalyst. In the investigation, attempts were made to perform the rearrangement in various conditions and also to carry out the hydrogenation with nickel catalyst.

EXPERIMENTAL

The condensation of the sugar with the amine and the rearrangement were carried out in a round-bottomed flask. The subsequent hydrogenation was performed in a pear-shaped glass vessel with a fused-on glass tube bent at a right-angle.



(I)



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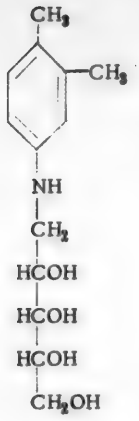

(III)

Energetic stirring was applied. The reaction temperature ranged from 80 to 95°.

5 g d-arabinose, 4 g 3,4-dimethylaniline and 0.25 g benzoic acid were heated on the water bath. The reaction period varied from 5 to 10 minutes. The dark solution was hydrogenated in presence of platinum in an alcoholic alkaline medium (using 2 ml 2N NaOH) until the full amount of hydrogen was absorbed. After completion of hydrogenation and removal of catalyst, the unreacted xylidine was removed by steam distillation. The aqueous solution in the distilling flask was concentrated to a small volume. The precipitate of d-ribamine was crystallized from butyl alcohol. M.p. 141-142°. Yield 1.0 to 1.3 g d-ribamine (12-14%). $[\alpha]_D^{16}$ + + 10° (using pyridine as solvent).

Isolation of 3,4-dimethylphenyl-d-arabinoside. 10 g d-arabinose, 8 g 3,4-dimethylaniline and 80 ml ethyl alcohol were heated to the boil under a reflux condenser for about an hour. Cooling resulted in separation from the filtrate of white crystals of the d-arabinoside with m.p. 125-126° (yield about 95-98%). The identity of the d-arabinoside was confirmed by preparation of d-arabinamine by hydrogenation in presence of platinum. M.p. 139-141° $[\alpha]_D^{18}$ + 10° (in pyridine).

Rearrangement of 3,4-dimethylphenyl-d-arabinoside. Attempts to isolate d-isoarabinosamine in the free state by rearrangement of the prepared d-arabinoside in a weakly acid medium at various pH values were unsuccessful. In all cases resinous bodies were obtained in which the presence of isoarabinosamine could only be detected qualitatively (reaction with 2,6-dichlorphenol-indophenol *). Small amounts of d-ribamine were isolated by hydrogenation of the resin.

Experiments on the rearrangement of d-arabinoside into d-isoarabinosamine in an alcoholic-acid medium under a hydrogen pressure of 100 atmospheres at 25-30° did not meet with success. Rearrangement of d-arabinoside in an alcoholic-acid medium in an autoclave under a hydrogen pressure of 50 atmospheres at 80-85° for 3 hours, followed by hydrogenation with nickel catalyst in a weakly alkaline medium, led in all cases to a mixture of d-ribamine and d-arabinamine, as was confirmed by the melting point and the specific rotation.

8 g d-arabinoside, 0.4 g benzoic acid and 25 ml 95% ethyl alcohol were heated in a rotating autoclave at 80-85° for 3 hours under a hydrogen pressure of 50 atmospheres. After cooling, addition was made to the autoclave of 25-30 ml ethyl alcohol (95%), 3-5 g nickel catalyst and 3 ml 2N NaOH. Hydrogenation was carried out for 6 hours at 60-65° with a hydrogen pressure of 25 atmospheres. A substance with m.p. 124-125° was isolated in a yield of 15-17% of the theoretical. $[\alpha]_D^{18}$ −13°.

Hydrogenation in a weakly acid medium. 10 g d-arabinose, 8 g 3,4-dimethylaniline, 0.4 g benzoic acid and 40 ml 95% alcohol were heated in a rotating autoclave at 80-85° under a hydrogen pressure of 50 atmospheres for an hour. Into the autoclave, after cooling, were introduced 5-6 g nickel catalyst and 30 ml alcohol. Hydrogenation was performed without addition of alkali in a weakly acid medium for 4 hours at 50-60° under a hydrogen pressure of 25 atmospheres.

* Isosaccharoamines possess the property of reducing certain dyes in the cold: for instance, methylene blue and 2,6-dichlorphenol-indophenol. On the other hand glucosides do not exhibit this property.

A compound with m.p. 134-135° was isolated in 35-40% yield. After recrystallization from butyl alcohol the m.p. was 138-139°; $[\alpha]_D^{18}$ −11° (in pyridine).

From the saccharoamine prepared by the last method was prepared an azo compound; this was condensed with barbituric acid to give a flavin dye [13] with m.p. 272° which rose to 290° after recrystallization (pure riboflavin melts at 290°, araboflavin at 302°).

Biological tests with the flavin dye on rats showed the activity to be half that of riboflavin (vitamin B_2). This once again confirms the possibility of contamination of the prepared product with arabinamine. Thus the araboflavin formed during the synthesis of the dye lowers the biological activity.

SUMMARY

1. 3,4-Dimethylphenyl-d-arabinoside was isolated in a yield of about 95-98% of the theoretical.

2. It was impossible to prepared 3,4-dimethylphenyl-d-isoarabinosamine in the free state by rearrangement of d-arabinoside at various pH values.

3. d-Arabinoside does not rearrange to d-isoarabinosamine under a hydrogen pressure of 100 atmospheres at 25-30°.

4. Rearrangement of d-arabinoside in an alcoholic acid medium in an autoclave under a hydrogen pressure of 50 atmospheres at 80-85° followed by hydrogenation with nickel catalyst in an alcoholic alkaline medium leads to a mixture of d-ribamine and d-arabinamine in a yield of 15-17% of the theoretical.

5. Rearrangement in an autoclave under pressure followed by hydrogenation with nickel catalyst in a weakly acid medium leads to a product consisting of d-ribamine and d-arabinamine in a yield of about 35-40% of the theoretical.

6. The synthesized flavin dye proved to possess one-half of the biological activity of riboflavin (vitamin B_2).

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Received March 15, 1951

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THE ALKAOIDS OF GALANTHUS WORONOWI

II. ISOLATION OF A NEW ALKALOID

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In the preceding paper on the alkaloids of Galanthus Woronowi (Amaryllidaceae family) one of us reported the isolation from the bulbs of this plant of two new alkaloids named galantine and galantidine. In the examination of the mother liquors after separation of these two alkaloids, we succeeded in isolating a third alkaloid which proved to be a base not previously described in the literature; we have named it galantamine.

The elementary analysis of galantamine leads to the formula $C_{17}H_{21}O_3N$. Galantamine is a fairly strong monoacidic base with m.p. 126-127° and a specific rotation of $[\alpha]_D$ −118.8°. It is very readily soluble in alcohol, acetone and chloroform; less easily soluble in benzene and ether; it is fairly soluble in hot water. It forms a series of well-crystallized salts: hydrochloride, m.p. 256-257°; hydrobromide, m.p. 246-247°; perchlorate, m.p. 223-224°; nitrate, m.p. 224-225°; chloroplatinate, m.p. 216-217°; all of these, like the base, are levorotary.

Galantamine contains a nonphenolic hydroxyl group, a methoxyl and a methylimino group. The third oxygen atom is in a reactive-inactive form. Consequently the formula of galantamine may be represented as $C_{15}H_{14}(NCH_3)(OCH_3)(OH)O$.

The presence of a hydroxyl group in galantamine was confirmed by the preparation of a monoacetyl derivative $C_{17}H_{20}O_3N(CH_3CO)$; m.p. 129-130°

The molecule of galantamine contains one double bond which is rather difficult to hydrogenate both with platinum catalyst (Adams) and with Raney nickel. Analysis of the hydrogenation product, m.p. 116-118°, corresponds to the formula $C_{17}H_{23}O_3N$. The melting points of dihydrogalantamine and of most of its derivatives are very close to those of galantamine and its corresponding derivatives, and the mixed samples for the most part do not exhibit any depression of melting point. However, the properties of dihydrogalantamine perchlorate and of such derivatives as the hydrobromide of the acetyl derivative and the perchlorate of the product of decomposition of dihydrogalantamine provided conclusive evidence of the presence of a hydrogenatable double bond in galantamine.

Methylation of glantamine with methyl iodide yielded a crystalline methyl iodide addition product with m.p. 278-279°; $[\alpha]_D$ −94.5°. Galantamine-methyl iodide very readily decomposes when heated with 25% alcoholic potassium hydroxide and forms a product with m.p. 80-82° whose elementary analysis corresponds to $C_{18}H_{23}O_3N$. The following salts were prepared to characterize the decomposition product: perchlorate, m.p. 221.5°-222.5°; picrate, m.p. 148-151°; methyl iodide compound, m.p. 188-189°.

EXPERIMENTAL

Extraction of the alkaloids. 25 kg dried and powdered bulbs of the Caucasian wild snowdrop are moistened with 7% ammonia solution and extracted with dichlorethane until the alkaloids are completely removed. The dichlorethane extract is extracted with 10% sulfuric acid. The sulfuric acid solution of the alkaloids is washed with ether to remove traces of dichlorethane and then made alkaline with ammonia.

Isolation of galantine and galantidine. After standing for a short period, the alkaline solution deposits a crystalline precipitate of galantine and galantidine (80.8 g) which is filtered at the pump and washed with water.

Separation of galantamine. The alkaline mother liquor, after separation of the crystalline alkaloids, is extracted with ether. The ether is distilled off to leave a yellow, viscous mass (58 g), from which by treatment with 10% hydrobromic acid solution, is deposited the crystalline hydrobromides of galantine and galantamine. The mixture of hydrobromides is washed and then digested with alcohol. The hydrobromide of galantine goes into solution in the alcohol while galantamine hydrobromide remains undissolved. Yield 22 g, m.p. 234-235°.

Recrystallization from water gives 20 g of galantamine hydrobromide with m.p. 246-247°.

3.315 mg substance: 6.786 mg CO_2; 2.021 mg H_2O. 3.439 mg substance: 6.994 mg CO_2; 2.021 mg H_2O. 3.322 mg substance: 1.753 mg AgBr. 3.267 mg substance: 1.713 mg AgBr. Found %: C 55.47, 55.65; H 6.59, 6.81; N 4.07, 3.8; Br 22.45, 22.31. $C_{17}H_{21}O_3N \cdot HBr$. Calculated %: C 55.45; H 5.98; N 3.8; Br 21.79. 0.1015 g substance in 15 ml water; $\underline{1}$ 1 dcm; α_D −0.63°; $[\alpha]_D$ −93.1°.

Separation of the base. 20 g galantamine hydrobromide (m.p. 246-247°) is dissolved in 15 ml water, made alkaline with ammonia and extracted with ether. Removal of the ether leaves 16 g light-yellow oil which soon crystallizes. The fine crystalline precipitate obtained by trituration with acetone is filtered at the pump and washed with acetone. Yield 12.8 g galantamine with m.p. 117-119°. After recrystallization from water or benzene the m.p. is 126-127°. 3.246 mg substance: 8.488 mg CO_2; 2.159 mg H_2O. 2.929 mg substance: 7.721 mg CO_2; 2.034 mg H_2O. 18.980 mg substance: 1.35 ml CH_4. 10.726 mg substance: 0.82 ml CH_4. Found %: C 71.32, 71.88; H 7.45, 7.65; N 4.93, 4.76; OH 4.98, 5.28. $C_{17}H_{21}O_3N$. Calculated %: C 71.08; H 7.315; N 4.87; OH 4.88.

0.1378 g substance in 10 ml alcohol; $\underline{1}$ 1 dcm; α_D −1.637°; $[\alpha]_D$ −118.8°.

Preparation of the salts. Galantamine nitrate. To 0.2 g galantamine with m.p. 126-127° is added 10% nitric acid solution until weakly acid. Rubbing with alcohol yields a finely crystalline precipitate of galantamine nitrate in amount of 0.2 g with m.p. 221-222.5°. Recrystallization from 3 ml alcohol gave 0.15 g with m.p. 224-225°.

3.267 mg substance: 6.847 mg CO_2; 1.785 mg H_2O. Found %: C 57.16; H 6.12. $C_{17}H_{21}O_3N \cdot HNO_3$. Calculated %: C 58.3; H 6.28.

Perchlorate. To a solution of 0.1 g galantamine in 1 ml 10% acetic acid is added a solution of the calculated amount of sodium perchlorate. After traces of acetic acid have been removed, by rubbing with alcohol a colorless finely crystalline precipitate is obtained; this is washed with alcohol and dried in a vacuum desiccator. Galantamine perchlorate melts at 223-224°.

Hydrochloride. Addition is made to galantamine of 5% hydrochloric acid solution until the reaction is weakly acid. The precipitate of hydrochloride is purified by crystallization from water; m.p. 256-257°.

Galantamine hydrochloride is very sparingly soluble in alcohol; it is quite insoluble in acetone; it dissolved with difficulty in cold water, more readily in hot.

Chloroplatinate. 0.1 g galantamine is dissolved in 1% hydrochloric acid, and to the solution is added dropwise a solution of platinum chloride. Fine yellow crystals of galantamine chlorplatinate are precipitated. After recrystallization from water the m.p. is 216-217°. The salt is very sparingly soluble in alcohol and rather more soluble in water.

Methyl iodide addition product. To a solution of 3 g galantamine in 60 ml acetone is added 6 ml methyl iodide; a white crystalline precipitate of galantamine-methyl iodide at once comes down. The reaction is completed by heating the mixture for 30 minutes. After cooling, the precipitate is filtered at the pump and washed with acetone. Yield 4.3 g methyl iodide with m.p. 254-255°.

After two recrystallizations from alcohol-water the methyl iodide addition product has m.p. 279°.

4.764 mg substance: 6.63 ml 0.01 N. $Na_2S_2O_3$. 5.320 mg substance: 7.40 ml 0.01 N $Na_2S_2O_3$. Found %: I 29.49, 29.46. $C_{17}H_{21}O_3N \cdot CH_3I$. Calculated %: I 29.6.

0.1002 g substance in 15 ml water; $\underline{1}$ 1 dcm; α_D −0.63°; $[\alpha]_D$ −94.5°.

Action of acetic anhydride on galantamine. 0.2 g galantamine is mixed with 2.5 ml pyridine and 2.5 ml acetic anhydride and the mixture heated on the water bath at 25-35°. After 5-10 minutes the precipitate goes into solution. Heating is continued for 12 hours. After vacuum distillation of the pyridine and excess of acetic anhydride, a 10% hydrobromic acid solution is added until the reaction is weakly acid. Treatment with acetone brings down white crystals of acetylgalantamine hydrobromide.

After three recrystallizations from alcohol-water the hydrobromide is in the form of beautiful large needles with m.p. 246-247°.

Acetylgalantamine is almost insoluble in alcohol and acetone, very soluble in water; a mixture with

galantamine hydrobromide has a depressed melting point of 242-244°. The acetylgalantamine base isolated from the hydrobromide melts at 129-130°; like the hydrobromide, it depresses the melting point of galantamine; the mixture melts at 94-96°.

3.482 mg substance: 8.809 mg CO_2; 2.139 mg H_2O. Found %: C 69.19; H 6.87. $C_{17}H_{19}O_3N(CH_3CO)$. Calculated %: C 69.30; H 6.99.

Action of alcoholic KOH on galantamine-methyl iodide. 3 g of galantamine-methyl iodide is mixed with 30 ml 25% potassium hydroxide solution in methyl alcohol and heated on the water bath for 45 minutes. On cooling, the reaction mixture is diluted with ether and separated from the alkaline solution; the ethereal solution is washed with 8 ml water to remove the alcohol and alkali, dried and distilled. The residue (2.06 g) after removal of the ether is a semiliquid, partly crystallizing oil which is triturated with ether. The precipitated crystals are filtered at the pump and washed with ether.

After recrystallization from petroleum ether there is obtained 1.44 g des-N-methylgalantamine with m.p. 80-82°.

3.485 mg substance: 9.209 mg CO_2; 2.291 mg H_2O. 3.172 mg substance: 8.370 mg CO_2; 2.060 mg H_2O. 6.350 mg substance: 0.276 ml N_2 (19.0°, 736.5 mm). 6.744 mg substance: 0.284 ml N_2 (21.0°, 728.6 mm). 9.834 mg substance: 0.77 ml CH_4. 10.916 mg substance: 0.85 ml CH_4. 7.887 mg substance: 7.70 ml $Na_2S_2O_3$ (0.02 N); 8.95 ml $Na_2S_2O_3$ (0.02 N). Found %: C 72.06, 71.96; H 7.35, 7.26; N 4.92, 4.69; OH 5.47, 5.44; OCH_3 10.09; NCH_3 10.98. $C_{16}H_{21}O_3N$. Calculated %: C 72.2; H 7.0; N 4.7; OH 5.6; OCH_3 10.23; NCH_3 9.57.

Picrate of des-N-methylgalantamine. Addition of picric acid solution to an aqueous solution of des-N-methylgalantamine leads to separation of a resin from which the aqueous mother liquor is decanted. Treatment of the resin with alcohol results in formation of a powdery precipitate. It is filtered at the pump and washed. The picrate melts at 148-151°.

Perchlorate. To 0.1 g des-N-methylgalantamine is added 5% hydrochloric acid solution until the reaction is weakly acid and a solution of 0.1 g sodium perchlorate. A turbidity appears, followed by a finely crystalline precipitate. After recrystallization from water 0.07 g perchlorate was obtained with m.p. 221.5-222.5°.

Methyl iodide addition product. 0.6 g des-N-methylgalantamine is dissolved in 30 ml acetone; 1.5 g methyl iodide is then added and the mixture heated for 30 minutes. After concentration to a small volume a crystalline precipitate of the methyl iodide is obtained and is twice recrystallized from alcohol to form rhombic plates (0.62 g) with m.p. 188-189°.

Catalytic hydrogenation of galantamine. 2 g galantamine is dissolved in 10% hydrochloric acid until weakly acid. The solution is agitated in a hydrogen atmosphere in presence of platinum oxide. 189 ml hydrogen is absorbed (one double bond requires 156 ml). The catalyst is filtered off and the solution treated with 25% ammonia and extracted with ether. The residue (2.12 g) after removal of the ether is a rather viscous oil with a light-yellow color. It is purified in the form of the hydrobromide.

The hydrobromide of dihyrogalantamine is almost completely insoluble in acetone, more readily soluble in alcohol from which it crystallizes in colorless, rather large crystals with m. p. 221.5-223°.

The isolated base is recrystallized from petroleum ether to give 0.72 g dihydrogalantamine with m.p. 116-118°.

3.369 mg substance: 8.774 mg CO_2; 2.462 mg H_2O. 6.408 mg substance: 0.273 ml N_2 (19.5°, 742.0 mm). 6.361 mg substance: 0.273 ml N_2 (19.5°, 742.0 mm). Found %: C 71.03; H 8.18; N 4.84, 4.89. $C_{17}H_{25}O_3N$. Calculated %: C 70.59; H 7.9; N 4.87.

Action of acetic anhydride on dihydrogalantamine. 0.35 g of hydrogenated galantamine is dissolved in 4.5 ml freshly distilled pyridine. To the solution is added 4.5 ml acetic anhydride and the mixture heated at 25-35° for 12 hours. After distilling off the pyridine and excess of acetic anhydride in vacuum, addition is made to the residue of 10% hydrobromic acid solution until the reaction is weakly acid. Treatment with acetone precipitates the hydrobromide of acetylated dihydrogalantamine which is filtered at the pump and washed with acetone.

The hydrobromide has m.p. 226-228° after recrystallization from alcohol.

4.105 mg substance: 8.325 mg CO_2; 2.400 mg H_2O. Found %: C 55.31; H 6.54. $C_{17}H_{22}O_3N(COCH_3)\cdot$ $\cdot HBr$. Calculated %: C 55.33; H 6.31.

SUMMARY

1. A new crystalline alkaloid with the composition $C_{17}H_{21}O_3N$ has been isolated from the bulbs of Galanthus Woronowi and has been given the name of galantamine.

2. Galantamine contains one hydroxyl, one methoxyl and one methylimino group. The third oxygen atom is in the reactive-inactive form.

3. Methylation of galantamine with methyl iodide gives the methyl iodide addition product.

4. Hofmann degradation of galantamine gives the decomposition product $C_{18}H_{23}O_3N$.

5. Methylation of the product of degradation of galantamine with methyl iodide gives its methyl iodide addition compound.

6. Galantamine is an unsaturated tertiary base. Hydrogenation yields dihydrogalantamine $C_{17}H_{23}O_3N$.

LITERATURE CITED

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Received October 7, 1950

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